IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In re Application of	)	
Sandra Helton McCain, et al.	)	Group: 1755
Serial No.: 10/783,896	)	
Filed: February 20, 2004	)	
Title: PIGMENT BLACK AND DILUTE DYE INKS IN INK SET	)	Examiner: V. Faison Gee

BRIEF OF APPELLANT

MS APPEAL BRIEF - PATENTS
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This appeal is taken from the decision of the Examiner, dated January 24, 2007, finally rejecting claims 5, 7, 11-14. Appellant timely filed a Notice of Appeal in this matter on April 20, 2007.

I. TABLE OF CONTENTS

II. REAL PARTY IN INTEREST

The real party in interest in this appeal is Lexmark International, Inc., a corporation organized and existing under the laws of the State of Delaware, which owns the entire interest in this patent application as set forth in the underlying claimed invention.

III. RELATED APPEALS AND INTERFERENCES

No related Appeals or Interferences are known to the Appellant.

IV. STATUS OF CLAIMS

Pending: 5, 7 and 11-14.

Canceled: 3, 4, 6, and 8

Allowed: None.

Objected To: None.

Rejected: 5, 7 and 11-14.

Withdrawn from Consideration: 1, 2, 9, and 10.

On Appeal: 5, 7 and 11-14.

V. STATUS OF AMENDMENTS

An Amendment under 37 CFR §1.116 requesting reconsideration was submitted in this case on March 28, 2007, in response to the final rejection in the Office Action mailed January 24, 2007. The claim amendments were not entered, as indicated in the Advisory Action mailed April 18, 2007.

VI. SUMMARY OF CLAIMED SUBJECT MATTER

The present Summary of Claimed Subject Matter includes background information in support of the claims, which is set forth immediately below, followed by a summary of each independent claim, including reference to Appellant's specification by page and line number, and reference to Appellant's drawings, which begins on page 8 of the present Brief.

A. Background Information

In the following background information, reference is made to the specification at the end of each paragraph.

The present invention relates to the combination of two dilute dye-based inks, such as dilute cyan and magenta inks, with polymer-dispersed pigmented black ink in the same printhead. (Spec at page 2, lines 13-15).

More particularly, this invention is such an ink set contained in separate compartments in a single ink jet printhead, all inks in that printhead being compatible with the black ink. This invention also encompasses a dye set of full intensity color inks separated from a printhead having at least two dilute dye-based inks and dispersant dispersed pigment ink. (Spec from page 2, line 24 to page 3, line 3).

Dilute inks in accordance with this invention typically have an optical density of 60% or less of the optical density of corresponding full strength ink (corresponding inks are inks of similar or identical color (hue)). Typical dilute inks have a dye content as essential colorant of 0.6 percent or less of the weight of the ink. Black pigments in accordance with this invention are typically standard carbon black, with the dispersant being a polymer which may take variety of forms. Self dispersed carbon blacks are known. These can add to overall density and the black pigment ink in accordance

with this invention may well be a mixture of self-dispersed carbon black and polymer-dispersed carbon black. (Spec at page 3, lines 4-12).

Referring to Fig. 1, the printhead 1 has three chambers 3, 5, and 7 in which two dilute color inks and one pigment black ink are kept. Similarly, in a separate cartridge the three chambers 3, 5, and 7 each contain full intensity inks of different colors. Orifices 9, 11, and 13 shown in FIG. 2 permit the ink in each chamber to leave the chamber for printing. Each orifice 9, 11, and 13 is in separate liquid communication with one of the chambers 3, 5, and 7. (Spec at page 8, lines 9-14).

Ink exits the printhead 1 from the same side (the side having orifices 9, 11, and 13 in FIG. 2) and generally from locations close together. Moreover, during non-use the printhead is brought to a location at which the exit ports are capped to prevent evaporation of the ink. Accordingly, inks in the typical printheads are subject to some moderate transfer of ink between chambers, such as chambers 3, 5, and 7. In accordance with this invention, the dilute inks must be compatible with the black inks in the moderate amounts which can be transferred across the printhead. (Spec at page 8, lines 18-24).

B. Claims

Claim 1 (claim 5 depends from claim 1). Referring to Figs. 1 and 2, an inkjet printhead 1 for inkjet printing comprising at least three separate chambers 3, 5 and 7, each of said chambers 3, 5 and 7 having an exit orifice 9, 11 and 13 (spec at page 8, lines 9-14),

wherein said printhead 1 contains an ink set, said ink set comprising at least three separate inks, each separate ink being contained in said separate chambers 3, 5 and 7 (spec at page 8, lines 9-10), said ink in said chambers 3, 5 or 7 being subject to some moderate entry of ink from other of said chambers 3, 5 and 7 (spec at page 8, lines 21-22), said ink set comprising:

a first dilute dye-based color ink of a first color in a first of said chambers 3, 5 and 7 (spec at page 2, lines 23-25, and page 8, lines 9-10),

a second dilute dye-based color ink of a second color in a second of said chambers 3, 5 and 7 (spec at page 2, lines 23-25, and page 8, lines 9-10), and

a black ink comprising black pigment dispersed in water in a third of said chambers 3, 5 and 7 (spec at page 2, lines 23-25, and page 8, lines 9-10),

said first ink and said second ink being compatible with said black ink when in said black ink in moderate amounts (spec at page 8, lines 23-24).

Claim 5. Referring to Figs. 1 and 2, an ink set for inkjet printing comprising the inkjet printhead 1 of claim 1 and further comprising at least one separate inkjet printhead 1 containing a first full intensity color ink having dye as colorant, a second full intensity color ink having dye as colorant, and a third full intensity color ink having dye as colorant (spec at page 3, lines 1-3 and page 8, lines 11-12).

VII. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

A. Claims 5 and 7 were rejected under 35 U.S.C. §102(b) as being anticipated by Takemoto, U.S. Patent No. 6,075,069.

B. Claims 5, 7 and 11-14 were rejected under 35 U.S.C. §102(b) as being anticipated by Kanaya et al., U.S. Patent No. 6,482,256.

VIII. ARGUMENT

CLAIMS 5, 7 AND 11-14 ARE PATENTABLE UNDER 35 U.S.C. 102(b)

A. In the Final Office Action mailed January 24, 2007, claims 5 and 7 were rejected under 35 U.S.C. §102(b) as being anticipated by Takemoto, U.S. Patent No. 6,075,069 (hereinafter Takemoto).

However, a claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference. Verdegaal Bros. v. Union Oil Co. of California, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987) (MPEP 2131).

As set forth below, Appellant submits that claims 5 and 7 are not disclosed, taught, or suggested by Takemoto, and are therefore patentable in their present respective forms.

1. Takemoto

Takemoto is directed to an in ink set and ink jet recording method. The ink jet recording method can realize a good color image having no significant feathering or bleeding, particularly bleeding derived from color-to-color intermixing. The ink set comprises a yellow ink, a magenta ink, a cyan ink, and optionally a black ink, the cyan ink comprising a resin emulsion, the yellow ink composition and the magenta ink composition comprising a reactant capable of breaking the state of dispersion and/or dissolution of a colorant and the resin emulsion in the cyan ink and the black ink (abstract).

In the ink set according to the first aspect of the Takemoto patent, the magenta ink composition and the cyan ink composition comprise a resin emulsion and/or an inorganic oxide colloid. When the black ink composition is contained in the ink set, the black ink

composition also preferably comprises a resin emulsion and/or an inorganic oxide colloid. Further, in the ink set according to this aspect of the Takemoto patent, the yellow ink composition comprises a reactant capable of breaking the dispersion and/or dissolution of the colorant and the resin emulsion and/or the inorganic oxide colloid in the magenta ink composition and the cyan ink composition (col. 3, lines 4-14).

In the ink set according to the second aspect of the Takemoto patent, the cyan ink composition comprises a resin emulsion and/or an inorganic oxide colloid. When the black ink composition is contained in the ink set, the black ink composition also preferably comprises a resin emulsion and/or an inorganic oxide colloid. Further, in this aspect of the Takemoto patent, the yellow ink composition and the magenta ink composition comprise a reactant capable of breaking the dispersion and/or dissolution of a colorant and the resin emulsion and/or the inorganic oxide colloid in the cyan ink composition. (col. 3, lines 15-25).

2. Claim 5 is not anticipated by Takemoto

Appellant's claim 5 is directed to an ink set for inkjet printing comprising at least two dilute color inks and a black ink, wherein the dilute color inks and the black ink are each in separate chambers in the same printhead.

In particular, Takemoto does not teach dilute color inks and a black ink each in separate chambers in the same printhead. This requirement is expressly claimed in dependent claim 5 as it contains all of the limitations from independent claim 1. Instead, Takemoto is directed to printing with reactive inks. Reactive inks in the same printhead are not consistent with the

objective of the present invention where the dilute inks are compatible with the black inks in the moderate amounts which can be transferred across the printhead.

In fact, Takemoto is silent as to how the inks are contained during printing. However, in the five tests described therein, Takemoto is clear in describing Tests 1, 3, and 4 that the black ink is printed after the color inks (note the language "to which the black ink was to be deposited" at col. 14, lines 4-5; and col. 15, lines 6-7 and 33-34). Test 5 refers to Test 1 for description and Test 2 prints black as a composite of color inks, not by a black ink.

Considering that the inks of Takemoto are reactive, it can not be inferred that they are necessarily in the same printhead since they would be so close together as to potentially react prematurely. Thus, Takemoto fails to expressly and/or inherently describe every element as set forth in claim 5.

In the Final Office Action, Response to Arguments, the Examiner asserts that the "limitation of the separate chambers in the same printhead, does not have an effect on the ink composition as claimed, nor is the Examiner reading these limitations as they do not relate to the ink composition as originally claimed."

Appellant respectfully disagrees with the Examiner's position. The Examiner may not simply ignore claim limitations in making a determination of anticipation under 35 U.S.C. §102(b). As set forth in MPEP 2131, "A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference." *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987); emphasis added. "The identical invention must be shown in as complete detail as is contained in the ... claim." *Richardson v. Suzuki Motor Co.*, 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989). The elements must be

arranged as required by the claim, but this is not an *ipsissimis verbis* test, i.e., identity of terminology is not required. *In re Bond*, 910 F.2d 831, 15 USPQ2d 1566 (Fed. Cir. 1990).

Since Takemoto does not disclose, teach, or suggest an ink set for inkjet printing comprising at least two dilute color inks and a black ink, wherein the dilute color inks and the black ink are each in separate chambers in the same printhead, and further wherein the dilute inks are compatible with the black inks in the moderate amounts which can be transferred across the printhead as recited in claim 5, for at least the reasons set forth above, each and every element as set forth in the claim is not found, either expressly or inherently described, in a single prior art reference, and hence, Takemoto does not anticipate claim 5.

Thus, for at least the reasons set forth above, Appellant submits that claim 5 is patentable in its present form.

Accordingly, Appellant respectfully requests that the Board reverse the rejection of claim 5 under 35 U.S.C. §102(b).

3. Claim 7 is not anticipated by Takemoto

Claim 7 further limits the ink set of claim 5 by specifying that the colorant of the first dilute color ink and the colorant of the second dilute color ink each is in amount to produce an optical density of less than 60% of the optical density of one of the full intensity inks having a corresponding color.

Claim 7 depends directly from claim 5. As set forth above with respect to claim 5, claim 5 is not anticipated by Takemoto. Claim 7 is thus believed to be allowable due to its dependence on otherwise allowable claim 5.

Thus, for at least the reasons set forth above, Appellant submits that claim 7 is patentable in its present respective form.

Accordingly, Appellant respectfully requests that the Board reverse the rejection of claim 7 under 35 U.S.C. §102(b).

B. In the Final Office Action mailed January 24, 2007, Claims 5, 7, 11 -14 were rejected under 35 U.S.C. §102(b) as being anticipated by anticipated by Kanaya et al., U.S. Patent No. 6,482,256 (hereinafter Kanaya et al.).

However, a claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference. Verdegaal Bros. v. Union Oil Co. of California, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987) (MPEP 2131).

As set forth below, Appellant submits that claims 5, 7 and 11-14 are not disclosed, taught, or suggested by Kanaya et al., and are therefore patentable in their present respective forms.

1. Kanaya et al.

Kanaya et al. is directed to an ink set which can realize images having good lightfastness and color reproduction. The ink set comprises magenta ink compositions, the magenta ink compositions containing specific compounds as colorants (abstract).

The ink set according to one aspect of the Kanaya et al. patent comprises two magenta ink compositions different from each other in color density. The ink set according to another aspect of the Kanaya et al. patent comprises a yellow ink composition, two magenta ink compositions different from each other in color density, and two cyan ink

compositions different from each other in color density. Alternatively, the ink set may comprise a yellow ink composition, a magenta ink composition with a single color density, and a cyan ink composition with a single color density. The two ink compositions different from each other in color density may be divided into an ink composition with higher color density and an ink composition with lower color density. (col. 6, lines 39-54).

2. Claim 5 is not anticipated by Kanaya et al.

Appellant's claim 5 is directed to an ink set for inkjet printing comprising at least two dilute color inks and a black ink, wherein the dilute color inks and the black ink are each in separate chambers in the same printhead.

In particular, Kanaya et al. does not teach dilute color inks and the black ink each in separate chambers in the same printhead. This requirement is expressly claimed in dependent claim 5 as it contains all of the limitations from independent claim 1. Instead, Kanaya et al. is directed to a magenta ink set comprising two magenta ink compositions different from each other in color density. Much of the description of Kanaya et al. does not even involve black ink, let alone the fact that the two color inks must be compatible with the black ink in the moderate amounts which can be transferred across the printhead, as recited in claim 5.

In summary, Kanaya et al. simply does not disclose expressly and/or inherently a pigment black in the same printhead with two dilute color inks as set forth in claim 5.

In the Final Office Action, Response to Arguments, the Examiner asserts that the "limitation of the separate chambers in the same printhead, does not have an effect on the ink composition as claimed, nor is the Examiner reading these limitations as they do not relate to the ink composition as originally claimed."

Appellant respectfully disagrees with the Examiner's position. The Examiner may not simply ignore claim limitations in making a determination of anticipation under 35 U.S.C. §102(b). As set forth in MPEP 2131, "A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference." *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987); emphasis added. "The identical invention must be shown in as complete detail as is contained in the ... claim." *Richardson v. Suzuki Motor Co.*, 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989). The elements must be arranged as required by the claim, but this is not an *ipsissimis verbis* test, i.e., identity of terminology is not required. *In re Bond*, 910 F.2d 831, 15 USPQ2d 1566 (Fed. Cir. 1990).

Since Kanaya et al. does not disclose, teach, or suggest an ink set for inkjet printing comprising at least two dilute color inks and a black ink, wherein the dilute color inks and the black ink are each in separate chambers in the same printhead, and further wherein the dilute inks are compatible with the black inks in the moderate amounts which can be transferred across the printhead as recited in claim 5, for at least the reasons set forth above, each and every element as set forth in the claim is not found, either expressly or inherently described, in a single prior art reference, and hence, Kanaya et al. does not anticipate claim 5.

Thus, for at least the reasons set forth above, Appellant submits that claim 5 is patentable in its present form.

Accordingly, Appellant respectfully requests that the Board reverse the rejection of claim 5 under 35 U.S.C. §102(b).

3. Claim 7 is not anticipated by Kanaya et al.

Claim 7 further limits the ink set of claim 5 by specifying that the colorant of the first dilute color ink and the colorant of the second dilute color ink each is in amount to produce an optical density of less than 60% of the optical density of one of the full intensity inks having a corresponding color.

Claim 7 depends directly from claim 5. As set forth above with respect to claim 5, claim 5 is not anticipated by Kanaya et al. Claim 7 is thus believed to be allowable due to its dependence on otherwise allowable claim 5.

Thus, for at least the reasons set forth above, Appellant submits that claim 7 is patentable in its present respective form.

Accordingly, Appellant respectfully requests that the Board reverse the rejection of claim 7 under 35 U.S.C. §102(b).

4. Claim 11 is not anticipated by Kanaya et al.

Claim 11 further limits the ink set of claim 5 by specifying that each of the first dilute color ink and the second dilute color ink have total color of dye in amount of 0.6 percent or less by weight of the ink of the dye.

Claim 11 depends directly from claim 5. As set forth above with respect to claim 5, claim 5 is not anticipated by Kanaya et al. Claim 11 is thus believed to be allowable due to its dependence on otherwise allowable claim 5.

Thus, for at least the reasons set forth above, Appellant submits that claim 11 is patentable in its present respective form.

Accordingly, Appellant respectfully requests that the Board reverse the rejection of claim 11 under 35 U.S.C. §102(b).

5. Claim 12 is not anticipated by Kanaya et al.

Claim 12 further limits the ink set of claim 11 by specifying that black pigment comprises carbon black.

Claim 12 depends directly from claim 11. As set forth above with respect to claim 11, claim 11 is not anticipated by Kanaya et al. Claim 12 is thus believed to be allowable due to its dependence on otherwise allowable claim 11.

Thus, for at least the reasons set forth above, Appellant submits that claim 12 is patentable in its present respective form.

Accordingly, Appellant respectfully requests that the Board reverse the rejection of claim 12 under 35 U.S.C. §102(b).

6. Claim 13 is not anticipated by Kanaya et al.

Claim 13 further limits the ink set of claim 7 by specifying that each of the first dilute color ink and the second dilute color ink have total color of dye in amount of 0.6 percent or less by weight of the ink of the dye.

Claim 13 depends directly from claim 7. As set forth above with respect to claim 7, claim 7 is not anticipated by Kanaya et al. Claim 13 is thus believed to be allowable due to its dependence on otherwise allowable claim 7.

Thus, for at least the reasons set forth above, Appellant submits that claim 13 is patentable in its present respective form.

Accordingly, Appellant respectfully requests that the Board reverse the rejection of claim 13 under 35 U.S.C. §102(b).

7. Claim 14 is not anticipated by Kanaya et al.

Claim 14 further limits the ink set of claim 13 by specifying that black pigment comprises carbon black.

Claim 14 depends directly from claim 13. As set forth above with respect to claim 13, claim 13 is not anticipated by Kanaya et al. Claim 14 is thus believed to be allowable due to its dependence on otherwise allowable claim 13.

Thus, for at least the reasons set forth above, Appellant submits that claim 14 is patentable in its present respective form.

Accordingly, Appellant respectfully requests that the Board reverse the rejection of claim 14 under 35 U.S.C. §102(b).

C. Conclusion

For the foregoing reasons, Appellant submits that claims 5, 7, and 11-14 are patentable in their present respective forms. Accordingly, Appellant respectfully requests that the Board reverse the final rejections of the appealed claims.

Respectfully submitted,

/Ronald K. Aust/

Ronald K. Aust
Registration No. 36,735

Attorney for Appellant

RKA15/ts

Electronically Filed: June 20, 2007

TAYLOR & AUST, P.C.
12029 E. Washington Street
Indianapolis, IN 46229
Telephone: 317-894-0801
Facsimile: 317-894-0803

IX. CLAIMS APPENDIX

1. (Withdrawn) An inkjet printhead for inkjet printing comprising at least three separate chambers, each of said chambers having an exit orifice,

wherein said printhead contains an ink set, said ink set comprising at least three separate inks, each separate ink being contained in said separate chambers, said ink in said chambers being subject to some moderate entry of ink from other of said chambers, said ink set comprising:

a first dilute dye-based color ink of a first color in a first of said chambers,

a second dilute dye-based color ink of a second color in a second of said chambers, and

a black ink comprising black pigment dispersed in water in a third of said chambers,

said first ink and said second ink being compatible with said black ink when in said black ink in moderate amounts.

2. (Withdrawn) The inkjet printhead of claim 1 in which each said first dilute color ink and said second dilute color ink have total color of dye in amount of 0.6 percent or less by weight of the ink of said dye.

3-4 (Canceled)

5. (Previously presented) An ink set for inkjet printing comprising the inkjet printhead of claim 1 and further comprising at least one separate inkjet printhead containing a first full intensity color ink having dye as colorant, a second full intensity color ink having dye as colorant, and a third full intensity color ink having dye as colorant.

6. (Canceled)

7. (Original) The ink set of claim 5 in which said colorant of said first dilute color ink and said colorant of said second dilute color ink each is in amount to produce an optical density of less than 60% of the optical density of one of said full intensity inks having a corresponding color.

8. (Canceled)

9. (Withdrawn) The inkjet printhead of claim 1 in which said colorant of said first dilute dye-based color ink and said colorant of said second dilute dye-based color ink each is in amount to produce an optical density of less than 60% of the optical density of a respective one of full intensity inks having a corresponding color.

10. (Withdrawn) The inkjet printhead of claim 1, and further comprising at least one separate inkjet printhead containing a first full intensity color ink having dye as colorant, a second full intensity color ink having dye as colorant, and a third full intensity color ink having dye as colorant, wherein said colorant of said first dilute dye-based color ink and said colorant of said second dilute dye-based color ink each is in amount to produce an optical density of less than 60% of the optical density of said full intensity inks having a corresponding color.

11. (Previously presented) The ink set of claim 5 in which each said first dilute color ink and said second dilute color ink have total color of dye in amount of 0.6 percent or less by weight of the ink of said dye.

12. (Previously presented) The ink set of claim 11 in which said black pigment comprises carbon black.

13. (Previously presented) The ink set of claim 7 in which each said first dilute color ink and said second dilute color ink have total color of dye in amount of 0.6 percent or less by weight of the ink of said dye.

14. (Previously presented) The ink set of claim 13 in which said black pigment comprises carbon black.

X. EVIDENCE APPENDIX

Included herein, and listed below, is a copy of each reference upon which the Examiner relied in rejecting one or more of the claims of the present application.

Exhibit:

A. U.S. Patent No. 6,075,069 (Takemoto).

B. U.S. Patent No. 6,482,256 (Kanaya et al.).

XI. RELATED PROCEEDINGS APPENDIX

(No Entries)

US006075069A

EXHIBIT A

United States Patent [19]

Takemoto

[11] Patent Number: 6,075,069

[45] Date of Patent: Jun. 13, 2000

[54] **COLOR INK JET RECORDING METHOD**

[75] Inventor: **Kiyohiko Takemoto**, Suwa, Japan

[73] Assignee: **Seiko Epson Corporation**, Tokyo-To, Japan

[21] Appl. No.: **08/935,605**

[22] Filed: **Sep. 23, 1997**

[30] **Foreign Application Priority Data**

Sep. 24, 1996 [JP] Japan 8-251948

[51] **Int. Cl.**[7] **C09D 11/00**; C09D 11/02

[52] **U.S. Cl.** **523/160**; 106/31.6

[58] **Field of Search** 523/160, 161; 347/15, 100; 106/31.27, 31.28, 31.29, 31.3, 31.59, 31.6, 31.61

[56] **References Cited**

U.S. PATENT DOCUMENTS

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5,439,957	8/1995	Takimoto et al.	524/101
5,485,188	1/1996	Tochihara et al.	347/100
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5,555,008	9/1996	Stoffel	347/100
5,560,771	10/1996	Takemoto et al.	106/31.49
5,614,007	3/1997	Kurabayashi et al.	106/31.27
5,679,139	10/1997	McInerney et al.	106/31.6
5,731,825	3/1998	Danzuka et al.	347/15
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0697445	2/1996	European Pat. Off. .
9118850	6/1997	Japan .

Primary Examiner—Vasu Jagannathan
Assistant Examiner—Callie E. Shosho
Attorney, Agent, or Firm—Ladas & Parry

[57] **ABSTRACT**

An ink set and a recording method, especially an ink jet recording method, are provided which can realize a good color image having no significant feathering or bleeding, particularly bleeding derived from color-to-color intermixing. The ink set comprises a yellow ink, a magenta ink, a cyan ink, and optionally a black ink, the cyan ink comprising a resin emulsion, the yellow ink composition and the magenta ink composition comprising a reactant capable of breaking the state of dispersion and/or dissolution of a colorant and the resin emulsion in the cyan ink and the black ink.

17 Claims, No Drawings

COLOR INK JET RECORDING METHOD

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an ink jet recording method, wherein two ink compositions are deposited onto a recording medium, and an ink set used therefor.

2. Background Art

An ink jet recording method is a printing method wherein droplets of an ink composition are ejected and deposited onto a recording medium such as paper. This method has a feature that an image having a high resolution and a high quality can be printed at a high speed with a relatively inexpensive apparatus. In general, the ink composition used in the ink jet recording comprises water as a main component and, added thereto, a colorant and a wetting agent such as glycerin added for prevention of clogging and other purposes.

On the other hand, a new ink jet recording method has been recently proposed which comprises applying a polyvalent metal salt solution onto a recording medium and then applying an ink composition containing a dye material having at least one carboxyl group (see e.g., Japanese Patent Laid-Open No. 202328/1993). The claimed advantage of this method is that polyvalent metal ions combine with the dye to form an insoluble composite which can provide an image having water resistance and a high quality free from color bleeding.

Further, an ink jet recording method has been proposed wherein a first ink composition containing a pH-sensitive dye is used in combination with a second ink composition having such a pH value as will cause precipitation of the pH-sensitive dye (Japanese Patent Laid-Open No. 208548/1993). The claimed advantage of this method is that use of these two ink compositions can realize an image having water resistance and high quality free from color bleeding.

Further, an ink jet recording method has been proposed wherein a color ink containing at least a surfactant or a penetrable solvent and a salt for imparting a penetrating property is used in combination with a black ink which cooperates with the salt to cause thickening or coagulation, thereby providing a high-quality color image having a high image density and free from color bleeding (Japanese Patent Laid-Open No. 106735/1994). More specifically, in this method, two liquids, i.e., a first liquid containing a salt and a second liquid of an ink composition, are printed to provide a good image.

Furthermore, other ink jet recording methods wherein two liquids are printed have been proposed, for example, in Japanese Patent Laid-Open Nos. 240557/1991 and 240558/1991.

SUMMARY OF THE INVENTION

The present inventors have now found that, in an ink jet recording method comprising printing such two liquids, use of in combination two ink compositions having specific compositions can realize a color image free from feathering or bleeding, particularly not having significant bleeding derived from color-to-color intermixing. The present invention has been made based on such finding.

Accordingly, an object of the present invention is to provide an ink set which can yield a good color image.

Another object of the present invention is to provide a recording method using this ink set which can realize a good color image.

According to the first aspect of the present invention, there is provided an ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition containing a magenta colorant, and a cyan ink composition containing a cyan colorant,

the magenta ink composition and the cyan ink composition each comprising a resin emulsion and/or an inorganic oxide colloid,

the yellow ink composition comprising a reactant capable of breaking the state of dispersion and/or dissolution of the colorant and the resin emulsion in the magenta ink composition and the cyan ink composition.

According to the second aspect of the present invention, there is provided an ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition containing a magenta colorant, and a cyan ink composition containing a cyan colorant,

the cyan ink composition comprising a resin emulsion and/or an inorganic oxide colloid,

the yellow ink composition and the magenta ink composition each comprising a reactant capable of breaking the state of dispersion and/or dissolution of the colorant and the resin emulsion in the cyan ink composition.

According to the third aspect of the present invention, there is provided an ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition having a lower color density containing a magenta colorant, a magenta ink composition having a higher color density containing a magenta colorant, a cyan ink composition having a lower color density containing a cyan colorant, and a cyan ink composition having a higher color density containing a cyan colorant,

the magenta ink composition having a lower color density, and the cyan ink composition having a lower color density each comprising a reactant capable of breaking the state of dispersion and/or dissolution of the colorant in the yellow ink composition, the magenta ink composition having a higher color density and the cyan ink composition having a higher color density.

According to the fourth aspect of the present invention, there is provided an ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition having a lower color density containing a magenta colorant, a magenta ink composition having a higher color density containing a magenta colorant, a cyan ink composition having a lower color density containing a cyan colorant, and a cyan ink composition having a higher color density containing a cyan colorant,

the yellow ink composition, the magenta ink composition having a lower color density, and the cyan ink composition having a lower color density each comprising a reactant capable of breaking the state of dispersion and/or dissolution of the colorant in the magenta ink composition having a higher color density and the cyan ink composition having a higher color density.

According to the fifth aspect of the present invention, there is provided a recording method using the above ink set of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Ink Sets According to First and Second Aspects of Invention

The ink sets according to the first and second aspects of the present invention each basically comprise a cyan ink composition. If necessary, it may further comprise a black

ink composition. The ink compositions constituting the ink set according to the present invention each comprise at least a colorant, water, and an organic solvent.

In the ink set according to the first aspect of the present invention, the magenta ink composition and the cyan ink composition comprise a resin emulsion and/or an inorganic oxide colloid. When the black ink composition is contained in the ink set, the black ink composition also preferably comprises a resin emulsion and/or an inorganic oxide colloid. Further, in the ink set according to this aspect of the present invention, the yellow ink composition comprises a reactant capable of breaking the dispersion and/or dissolution of the colorant and the resin emulsion and/or the inorganic oxide colloid in the magenta ink composition and the cyan ink composition.

In the ink set according to the second aspect of the present invention, the cyan ink composition comprises a resin emulsion and/or an inorganic oxide colloid. When the black ink composition is contained in the ink set, the black ink composition also preferably comprises a resin emulsion and/or an inorganic oxide colloid. Further, in this aspect of the present invention, the yellow ink composition and the magenta ink composition comprise a reactant capable of breaking the dispersion and/or dissolution of a colorant and the resin emulsion and/or the inorganic oxide colloid in the cyan ink composition.

The ink sets according to the present invention can realize a good color image. A major cause of a deterioration in quality of a color image is uneven color mixing at boundary areas between different colors, i.e., color bleeding. According to the ink composition of the present invention, the color bleeding can be effectively prevented. The ink composition containing a reactant, upon contact on a recording medium with the ink composition containing a colorant and a resin emulsion of which the state of dispersion and/or dissolution is broken by the reactant, agglomerates the colorant and the resin emulsion and the inorganic oxide colloid, after which color mixing caused by flow of the ink composition is prevented.

The ink compositions containing a reactant in the ink set according to the present invention, i.e., the yellow ink composition in the first aspect of the present invention and the yellow and magenta ink compositions in the second aspect of the present invention, each basically comprise a colorant, water, a water-soluble organic solvent, and a reactant.

As described above, the reactant according to the present invention is not particularly limited so far as it can break the state of dispersion and/or dissolution of the colorant and the resin emulsion and/or the inorganic oxide colloid in the ink composition free from the reactant. However, specific examples of preferred reactants usable herein include polyvalent metal salts, polyallylamine, and polyallylamine derivatives.

Preferred examples of a polyvalent metal salt as a reactant include salts which are constituted by divalent or higher polyvalent metallic ions and anions bonded to the polyvalent metallic ions and are soluble in water. Specific examples of polyvalent metallic ions include divalent metallic ions, such as Ca^{2+}, Cu^{2+}, Ni^{2+}, Mg2+, Zn^{2+}, and Ba^{2+}, trivalent metallic ions, such as Al^{3+}, Fe^{3+}, and Cr^{3+}. Anions include Cl^-, NO^{3-}, I^-, Br^-, ClO_3^-, and CH_3COO^-.

In particular, a metal salt constituted by Ca^{2+} or Mg^{2+} provides favorable results in terms of pH of the first solution and the quality of prints.

The concentration of the polyvalent metal salt in the ink composition may be suitably determined so as to attain the effect of providing a good print quality and preventing clogging. It, however, is preferably about 0.1 to 40% by weight, more preferably about 5 to 25% by weight.

According to a preferred embodiment of the present invention, the polyvalent metal salt is constituted by divalent or higher polyvalent metallic ions and nitrate ions or carboxylate ions bonded to the polyvalent metallic ions and is soluble in water.

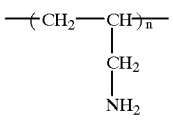
The carboxylate ions are preferably derived from a saturated aliphatic monocarboxylic acid having 1 to 6 carbon atoms and a carbocyclic monocarboxylic acid having 7 to 11 carbon atoms. Preferred examples of the saturated aliphatic monocarboxylic acid having 1 to 6 carbon atoms include formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, pivalic acid, and hexanoic acid. Among them, formic acid and acetic acid are particularly preferred.

A hydrogen atom(s) on the saturated aliphatic hydrocarbon residue in the monocarboxylic acid may be substituted by a hydroxyl group. Preferred examples of such carboxylic acids include lactic acid.

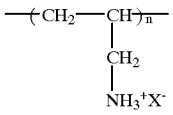
Preferred examples of the carbocyclic monocarboxylic acid having 6 to 10 carbon atoms include benzoic acid and naphthoic acid with benzoic acid being more preferred.

The polyallylamine and polyallylamine derivative, which may be preferably used as the reactant, are cationic polymers which are soluble in water and can be positively charged in water. Such polymers include, for example, those represented by the following formulae (a), (b), and (c):

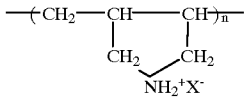
(a)



(b)



(c)



wherein X^- represents chloride, bromide, iodide, nitrate, phosphate, sulfate, acetate or other ion.

In addition, a copolymer of an allylamine with a diallylamine and a copolymer of diallylmethylammonium chloride with sulfur dioxide may also be used.

The content of the polyallylamine and the polyallylamine derivative is preferably 0.5 to 10% by weight based on the ink composition.

Various colorants may be used as the colorant contained in the ink composition containing a reactant in the ink set according to the present invention so far as they are not agglomerated by the reactant. The colorant used in these ink compositions may be either a dye or a pigment. According to a preferred embodiment of the present invention, the above pigment is preferably added, to the ink, in the form of a pigment dispersion prepared by dispersing the pigment in an aqueous medium with the aid of a dispersant or a surfactant. Preferred dispersants include those commonly used in the preparation of a dispersion of a pigment, for example, polymeric dispersant.

Preferred example of dispersant include cationic dispersants, anionic dispersants, and nonionic dispersants. Preferred examples of anionic dispersants usable herein include polyacrylic acid, polymethacrylic acid, acrylic acid/acrylonitrile copolymer, vinyl acetate/acrylic ester copolymer, acrylic acid/alkyl acrylate copolymer, styrene/acrylic acid copolymer, styrene/methacrylic acid copolymer, styrene/acrylic acid/alkyl acrylate copolymer, styrene/methacrylic acid/alkyl acrylate copolymer, styrene/α-methylstyrene/acrylic acid copolymer, styrene/α-methylstyrene/acrylic acid/alkyl acrylate copolymer, styrene/maleic acid copolymer, vinylnaphthalene/maleic acid copolymer, vinyl acetate/ethylene copolymer, vinyl acetate/fatty acid/vinylethylene copolymer, vinyl acetate/maleic ester copolymer, vinyl acetate/crotonic acid copolymer, and vinyl acetate/acrylic acid copolymer. Preferred examples of the anionic dispersant include sodium dodecylbenzenesulfonate, sodium laurate and an ammonium salt of a polyoxyethylene alkyl ether sulfate. Further, preferred examples of the nonionic dispersant include a polyoxyethylene alkyl ether, a polyoxyethylene alkyl ester, a polyoxyethylene sorbitan fatty acid ester, a polyoxyethylene alkyl phenyl ether, a polyoxyethylene alkylamine, and a polyoxyethylene alkylamide. They may be used alone or as a mixture of two or more. Further, it is also possible to use commercially available nonionic dispersants such as OLFINE Y and Surfynol 82, 104, 440, 465, 485 and TG (all the above products being acetylene glycol and manufactured by Air Products and Chemicals Inc.) and Solsperse 27000 (manufactured by Zeneca Co., Ltd.

According to a preferred embodiment of the present invention, the nonionic dispersant is preferable, especially when a polyvalent metal salt is used as a reactant. The use of the nonionic dispersant can realize a good storage stability of the ink composition. Furthermore, the use of the nonionic dispersant can realize a stable printing for long time in ink Jet printing with a piezoelectric recording head.

According to a further preferred embodiment of the present invention, when the ink composition that contains a reactant include a nonionic dispersant, the ink composition that is free from a reactant preferably include an anionic dispersant.

Specific examples of organic solvents usable herein include high-boiling organic solvents. The high-boiling organic solvent serves to prevent the ink composition from being concentrated due to evaporation, thus preventing clogging of a recording head. Preferred examples of high-boiling organic solvents include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, propylene glycol, butylene glycol, 1,2,6-hexanetriol, thioglycol, hexylene glycol, glycerin, trimethylolethane, and trimethylolpropane; alkyl ethers of polyhydric alcohols, such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, and triethylene glycol monobutyl ether; urea, 2-pyrrolidone, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, and triethanolamine.

Although the amount of the high-boiling organic solvent added is not particularly limited, it is preferably about 0.5 to 40% by weight, more preferably about 2 to 20% by weight.

The reactant-containing ink composition may contain a low-boiling organic solvent as the organic solvent. Preferred examples of low-boiling organic solvents usable herein include methanol, ethanol, n-propyl alcohol, isopropyl alcohol, n-butanol, sec-butanol, tert-butanol, isobutanol, and n-pentanol. Monohydric alcohols are particularly preferred. The low-boiling organic solvent has the effect of shortening the time taken for drying the ink. The amount of the low-boiling organic solvent added is preferably in the range of from 0.5 to 10% by weight, more preferably in the range of from 1.5 to 6% by weight.

According to a preferred embodiment of the present invention, the reactant-containing ink composition may contain a penetrating agent. Penetrating agents usable herein include various surfactants such as anionic, cationic, and amphoteric surfactants; alcohols such as methanol, ethanol, and iso-propyl alcohol; and lower alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, propylene glycol monobutyl ether, and dipropylene glycol monobutyl ether.

The ink compositions, containing a resin emulsion and/or an inorganic oxide colloid, constituting the ink set according to the present invention, that is, the magenta and cyan ink compositions in the first aspect of the present invention and the cyan ink compositions in the second aspect of the present invention, each basically comprise a colorant, water, a water-soluble organic solvent, and a resin emulsion and/or an inorganic oxide colloid.

The colorant used in these ink compositions may be either a dye or a pigment so far as the state of the dispersion and/or dissolution can be broken by the reactant. The pigment, however, is preferred.

Dyes usable herein include various dyes commonly used in ink compositions, especially ink jet recording, such as direct dyes, acid dyes, foodstuff dyes, basic dyes, reactive dyes, disperse dyes, vat dyes, soluble vat dyes, and reactive disperse dyes.

Regarding the pigment, inorganic and organic pigments are usable without any particular limitation. Examples of the inorganic pigment include, in addition to titanium oxide and iron oxide, carbon blacks produced by known processes, such as contact, furnace, and thermal processes. Examples of the organic pigment include azo pigments (including azo lake, insoluble azo pigment, condensed azo pigment, and chelate azo pigment), polycyclic pigments (for example, phthalocyanine, perylene, perinone, anthraquinone, quinacridone, dioxazine, thioindigo, isoindolinone, and quinophthalone pigments), dye chelates (for example, basic dye chelates and acid dye chelates), nitro pigments, nitroso pigments, and aniline black.

According to a preferred embodiment of the present invention, the above pigment is preferably added, to the ink, in the form of a pigment dispersion prepared by dispersing the pigment in an aqueous medium with the aid of a dispersant or a surfactant. Preferred dispersants include those commonly used in the preparation of a dispersion of a pigment, for example, polymeric dispersant. Preferred examples of the dispersant may include dispersants listed in connection with the ink composition containing a reactant.

According to a preferred embodiment of the present invention, as described above, the ink composition that is free from a reactant preferably includes an anionic dispersant when the ink composition that contains a reactant includes a nonionic dispersant.

Preferred examples of the anionic dispersant usable herein include polyacrylic acid, polymethacrylic acid, acrylic acid/acrylonitrile copolymer, vinyl acetate/acrylic ester copolymer, acrylic acid/alkyl acrylate copolymer, styrene/acrylic acid copolymer, styrene/methacrylic acid copolymer, styrene/acrylic acid/alkyl acrylate copolymer, styrene/

methacrylic acid/alkyl acrylate copolymer, styrene/a-methylstyrene/acrylic acid copolymer, styrene/α-methylstyrene/acrylic acid/alkyl acrylate copolymer, styrene/maleic acid copolymer, vinylnaphthalene/maleic acid copolymer, vinyl acetate/ethylene copolymer, vinyl acetate/fatty acid/vinylethylene copolymer, vinyl acetate/maleic ester copolymer, vinyl acetate/crotonic acid copolymer, and vinyl acetate/acrylic acid copolymer.

According to a preferred embodiment of the present invention, the weight average molecular weight of the copolymer is preferably about 3,000 to 50,000, more preferably about 5,000 to 30,000, most preferably about 7,000 to 15,000.

The dispersant added may be added in any amount so far as the pigment can be stably dispersed and the other effects of the present invention are not lost. According to a preferred embodiment of the present invention, the amount of the dispersant added is preferably in the range of from about 1:0.06 to 1:3, more preferably in the range of from about 1:0.125 to 1:3, in terms of the ratio of the pigment to the dispersant.

In this connection, that the dispersant and the surfactant contained in the dispersion of the pigment function also as the dispersant and the surfactant for the ink composition will be apparent to a person having ordinary skill in the art.

The amount of the pigment added to the ink is preferably about 0.5 to 25% by weight, more preferably about 2 to 15% by weight.

The resin emulsion contained in the ink composition refers to an emulsion comprising water as a continuous phase and the following resin component as a dispersed phase. Resin components as the dispersed phase include acrylic resin, vinyl acetate resin, styrene/butadiene resin, vinyl chloride resin, (meth)acrylate/styrene resin, butadiene resin, styrene resin, crosslinked acrylic resin, crosslinked styrene resin, benzoguanamine resin, phenolic resin, silicone resin, and epoxy resin.

According to a preferred embodiment of the present invention, the resin is a polymer having a combination of a hydrophilic segment with a hydrophobic segment. The particle diameter of the resin component is not particularly limited so far as the resin component can form an emulsion. It, however, is preferably not more than about 150 nm, more preferably about 5 to 100 nm.

The resin emulsion may be prepared by dispersion polymerization of a resin monomer, optionally together with a surfactant, in water. For example, an emulsion of an acrylic resin or a styrene/acrylic resin may be prepared by subjecting an ester of (meth)acrylic acid or alternatively an ester of (meth)acrylic acid in combination with styrene to dispersion polymerization in water in the presence of a surfactant. In general, the mixing ratio of the resin component to the surfactant is preferably about 10:1 to 5:1. When the amount of the surfactant used falls within the above range, it is possible to provide an ink which has good water resistance in the form of an image and good penetrability. The surfactant is not particularly limited. Preferred examples thereof include anionic surfactants (for example, sodium dodecylbenzenesulfonate, sodium laurate and an ammonium salt of a polyoxyethylene alkyl ether sulfate); nonionic surfactants (for example, a polyoxyethylene alkyl ether, a polyoxyethylene alkyl ester, a polyoxyethylene sorbitan fatty acid ester, a polyoxyethylene alkyl phenyl ether, a polyoxyethylene alkylamine, and a polyoxyethylene alkylamide). They may be used alone or as a mixture of two or more. Further, it is also possible to use acetylene glycol (OLFINE Y and Surfynol 82, 104, 440, 465, 485 and TG (all the above products being manufactured by Air Products and Chemicals Inc.).

The ratio of the resin as the component constituting the dispersed phase to water is suitably 60 to 400 parts by weight based on 100 parts by weight of the resin with 100 to 200 parts by weight, based on 100 parts by weight of the resin, of water being preferred.

Known resin emulsions may also be used as the above resin emulsion. For example, resin emulsions described in Japanese Patent Publication No. 1426/1987 and Japanese Patent Laid-Open Nos. 56573/1991, 79678/1991, 160068/1991, and 18462/1992 as such may be used as the resin emulsion in the present invention.

Further, commercially available resin emulsions may also be used, and examples thereof include Microgel E-1002 and E-5002 (styrene/acrylic resin emulsion, manufactured by Nippon Paint Co., Ltd.), Voncoat 4001 (acrylic resin emulsion, manufactured by Dainippon Ink and Chemicals, Inc.), Voncoat 5454 (styrene/acrylic resin emulsion, manufactured by Dainippon Ink and Chemicals, Inc.), SAE-1014 (styrene/acrylic resin emulsion, manufactured by Nippon Zeon Co., Ltd.), and Saivinol SK-200 (acrylic resin emulsion, manufactured by Saiden Chemical Industry Co., Ltd.).

According to a preferred embodiment of the present invention, the amount of the resin emulsion incorporated therein is preferably such that the amount of the resin component is in the range of from 0.1 to 40% by weight, more preferably in the range of from 1 to 25% by weight.

The resin emulsion, by virtue of interaction with the reactant, has the effect of preventing the creation of color bleeding and, at the same time, inhibiting the penetration of a coloring component and, further, accelerating the fixation on the recording medium. Further, some resin emulsions have an additional effect that they form a film on the recording medium to improve the rubbing resistance of the resultant print.

The ink composition used in the present invention may contain an inorganic oxide colloid. Preferred examples of inorganic oxide colloids usable herein include colloidal silica and alumina colloid. These are generally a colloidal solution of ultrafine particles of SiO_2, Al_2O_3 or the like in water or an organic solvent. Commercially available inorganic oxide colloids are generally such that the dispersion medium is water, methanol, 2-propanol, n-propanol, xylene or the like and the diameter of SiO_2, Al_2O_3 and other particles is 5 to 100 nm. Further, pH of the colloidal solutions of inorganic oxide is, in many cases, adjusted to the acidic or alkaline side rather than the neutral region. This is because the stable dispersion region of the inorganic oxide colloid is present on the acidic side or the alkaline side. In adding the colloidal solution to the ink composition, pH of the stable dispersion region of the inorganic oxide colloid and pH of the ink should be taken into consideration.

The amount of the inorganic oxide colloid added to the ink composition is preferably 0.1 to 15% by weight, and addition of two or more inorganic oxide colloids is also possible.

According to a preferred embodiment of the present invention, the ink composition comprising a resin emulsion and/or an inorganic oxide colloid preferably comprises an alginic acid derivative. Preferred examples of alginic acid derivatives include alkali metal salts (for example, sodium salt and potassium salt) of alginic acid, organic acid salts (for example, triethanolamine salt) of alginic acid, and ammonium alginate.

The amount of the alginic acid derivative added to the ink composition is preferably about 0.01 to 1% by weight, more preferably about 0.05 to 0.5% by weight.

Although the reason why a good image can be formed by the addition of an alginic acid derivative has not been elucidated yet, it is considered that the reactant, particularly the polyvalent metal salt, reacts with the alginic acid derivative in the ink composition to vary the dispersed state of the colorant, promoting the agglomeration and fixation of the colorant onto the recording medium.

According to a preferred embodiment of the present invention, the ink composition comprising a resin emulsion and/or an inorganic oxide colloid preferably contains an organic solvent. The organic solvent is preferably a low-boiling organic solvent, and preferred examples thereof include methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, sec-butanol, tert-butanol, iso-butanol, and n-pentanol. Monohydric alcohols are particularly preferred. The low-boiling organic solvent has the effect of shortening the time taken for drying the ink.

Further, according to a preferred embodiment of the present invention, the ink composition comprising a resin emulsion and/or an inorganic oxide colloid further comprises a wetting agent comprising a high-boiling organic solvent. Preferred examples of high-boiling organic solvents usable herein include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, propylene glycol, butylene glycol, 1,2,6-hexanetriol, thioglycol, hexylene glycol, glycerin, trimethylolethane, and trimethylolpropane; alkyl ethers of polyhydric alcohols, such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, and triethylene glycol monobutyl ether; urea; 2-pyrrolidone; N-methyl-2-pyrrolidone; 1,3-dimethyl-2-imidazolidinone; and triethanolamine.

The amount of the wetting agent added is preferably in the range of from 0.5 to 40% by weight, more preferably in the range of from 2 to 20% by weight, based on the ink. The amount of the low-boiling organic solvent added is preferably 0.5 to 10% by weight, more preferably in the range of from 1.5 to 6% by weight, based on the ink.

According to a preferred embodiment of the present invention, the ink composition comprising a resin emulsion and/or an inorganic oxide colloid contains a saccharide. Examples of saccharides usable herein include monosaccharides, disaccharides, oligosaccharides (including trisaccharides and tetrasaccharides), and other polysaccharides, preferably glucose, mannose, fructose, ribose, xylose, arabinose, galactose, aldonic acid, glucitol, sorbitol, maltose, cellobiose, lactose, sucrose, trehalose, and maltotriose. The term "polysaccharide" used herein refers to saccharides, in a broad sense, including substances which widely exist in the natural world, such as alginic acid, a-cyclodextrin, and cellulose.

Derivatives of these saccharides include reducing sugars of the above saccharides (for example, sugar alcohols represented by the general formula $HOCH_2(CHOH)_nCH_2OH$ wherein n is an integer of 2 to 5), oxidized sugars (for example, aldonic acid and uronic acid), amino acid, and thiosugars. Sugar alcohols are particularly preferred, and specific examples thereof include maltitol and sorbitol.

The content of the above saccharide is suitably in the range of from 0.1 to 40% by weight, preferably 0.5 to 30% by weight, based on the ink.

Further, the ink compositions constituting the ink set according to the present invention may, if necessary, contain pH adjustors, preservatives, antimolds and the like.

Ink Set According to Third and Fourth Aspects of Invention

The ink set according to the third or fourth aspect of the present invention comprises a yellow ink composition, two magenta ink compositions different from each other in color density, two cyan ink compositions different from each other in color density, and optionally a black ink composition.

In the third aspect of the present invention, a reactant is added to the magenta ink having a lower color density (hereinafter often referred to as "light-colored magenta ink") and the cyan ink composition having a lower color density (hereinafter often referred to as "light-colored cyan ink"). Further, the fourth aspect of the present invention, a reactant is added to the yellow ink composition, a light-colored magenta ink and a light-colored cyan ink. In the ink set of the third or fourth aspect of the present invention, what is required of the reactant is to break the state of dispersion and/or dissolution of the colorant contained in at least the magenta ink composition having a higher color density, a cyan ink composition having a higher color density, and, the yellow ink composition in the case of the fourth aspect of the present invention, and optionally, the black ink composition.

According to a preferred embodiment of the present invention, in the third and fourth aspects of the present invention, the ink composition that is free from a reactant may include a resin emulsion and/or an inorganic oxide colloid, and the reactant can break the state of dispersion and/or dissolution of the resin emulsion and/or the inorganic oxide colloid. In particular, in the third aspect of the present invention, the yellow ink composition, the magenta ink composition having a higher color density, the cyan ink composition having a higher color density, and, if necessary, the black ink composition comprise a resin emulsion and/or an inorganic oxide colloid. In the fourth aspect of the present invention, the magenta ink composition having a higher color density, the cyan ink composition having a higher color density, and, if necessary, the black ink composition comprise a resin emulsion and/or an inorganic oxide colloid.

As with the ink sets according to the first and second aspects of the present invention, the ink set according to the third and fourth aspects of the present invention can provide a good color image.

Components of the ink compositions constituting the ink set according to the third and fourth aspects of the present invention may be substantially the same as those of the ink compositions constituting the ink sets according to the first and second aspects of the present invention. The difference in color density between ink compositions different from each other in color density may be created by making the dye concentration of one ink composition lower or higher than that of the other ink composition or alternatively by suitably selecting the kind of the colorant used.

Ink Set According to Fifth Aspect of Invention

The ink set according to the fifth aspect of the present invention comprises a yellow ink composition, a magenta ink composition, a cyan ink composition and a black ink composition. Further, the black ink composition comprises a resin emulsion and/or an inorganic oxide colloid, and the yellow ink composition, the magenta ink composition, and cyan ink composition each comprises a reactant capable of breaking the state of dispersion and/or dissolution of the colorant and the resin emulsion in the black ink composition.

As with the ink sets according to the first and second aspects of the present invention, the ink set according to the fifth aspect of the present invention can provide a good color image.

Components of the ink compositions constituting the ink set according to the fifth aspect of the present invention may

be substantially the same as those of the ink compositions constituting the ink sets according to the first and second aspects of the present invention.

Ink Jet Recording Method

The ink sets according to the present invention are used in recording methods using an ink composition. Recording methods using an ink composition include, for example, an ink jet recording method, a recording method using writing utensils, such as pens, and other various printing methods. Particularly preferably, the ink compositions according to the present invention are used in the ink jet recording method.

Thus, according to another aspect of the present invention, there is provided an ink jet recording method using the ink set of the present invention. According to the ink jet recording method, the sequence of printing of the ink compositions is not particularly limited. Specifically, the ink composition containing a reactant may be first printed onto a recording medium followed by printing of the ink composition containing a colorant and a resin emulsion which can be agglomerated by the reactant, or vice versa.

According to a preferred embodiment of the present invention, the mass of the droplet of the ink composition ejected is regulated so that the size of a pixel formed by the ink composition that contains a reactant is smaller than a pixel formed by the ink composition that is free from a reactant. More specifically, the mass of the droplet of the ink composition that contains a reactant is preferably less than 30 to 100% by weight of the mass of the droplet of the ink composition that is free from a reactant. This can realize a better image, especially an image with minimized feathering or color bleeding.

EXAMPLES

The present invention will be described in more detail with reference to the following examples, though it is not limited to these examples only.

The following ink compositions were prepared according to a conventional method. Specifically, a colorant component, together with a dispersant component, was dispersed. After other components were added thereto, they were mixed together. Insolubles having a given size or larger were removed by filtration to give an ink composition.

Yellow ink 1	
C.I. Pigment Yellow 17	2 wt %
Solsperse 27000 (nonionic dispersant, manufactured by Zeneca Co., Ltd.)	1 wt %
Sucrose	0.7 wt %
Maltitol	6.3 wt %
Glycerin	10 wt %
2-Pyrrolidone	2 wt %
Surfynol TG	1 wt %
Magnesium nitrate hexahydrate (reactant)	5 wt %
Pure water	Balance

Yellow ink 2	
C.I. Acid Yellow 23	3 wt %
Diethylene glycol	10 wt %
Surfynol TG	1 wt %
Polyallylamine PAA-10C (reactant, resin component 10%, manufactured Nitto Boseki Co., Ltd.)	30 wt %
Pure water	Balance

-continued

Yellow ink 3	
C.I. Pigment Yellow 74	2 wt %
Styrene/acrylic copolymer ammonium salt (nonionic dispersant)	1 wt %
Grandoll Pp-1000 (styrene/acrylic resin emulsion, resin component 45%, manufactured by Dainippon Ink and Chemicals, Inc.)	5 wt %
Alumina Sol 200 (Al_2O_3 content 10%, manufactured by Nissan Chemical Industry Ltd.)	5 wt %
Maltitol	10 wt %
Glycerin	10 wt %
2-Pyrrolidone	2 wt %
Surfynol TG	1 wt %
Pure water	Balance

Magenta ink 1	
C.I. Pigment Red 57:1	2 wt %
Solsperse 27000 (nonionic dispersant)	1 wt %
Sucrose	10 wt %
Glycerin	5 wt %
Triethanolamine	2 wt %
Surfynol TG	1 wt %
Calcium chloride (reactant)	8 wt %
Pure water	Balance

Magenta ink 2	
C.I. Direct Red 9	3 wt %
Diethylene glycol	10 wt %
Surfynol TG	1 wt %
Polyallylamine PAA-10C (reactant)	30 wt %
Pure water	Balance

Magenta ink 3	
C.I. Pigment Red 122	3 wt %
Styrene/acrylic copolymer ammonium salt (anionic dispersant)	1 wt %
Microgel E-5002 (styrene/acrylic resin emulsion, resin component 29.2%, MFT = about 80° C., manufactured by Nippon Paint Co., Ltd.)	3.5 wt %
Sucrose	0.7 wt %
Maltitol	6.3 wt %
Glycerin	10 wt %
2-Pyrrolidone	2 wt %
Surfynol TG	1 wt %
Pure water	Balance

Light-colored magenta ink 1	
C.I. Pigment Red 122	0.5 wt %
Solsperse 27000 (nonionic dispersant)	0.3 wt %
Diethylene glycol	10 wt %
Surfynol TG	1 wt %
Ammonium hydroxide	1 wt %
Magnesium sulfate tetrahydrate (reactant)	10 wt %
Pure water	Balance

Cyan ink 1	
C.I. Direct Blue 199	3 wt %
Snowtex S (colloidal silica, SiO_2 content 30%, manufactured by Nissan Chemical Industry Ltd.)	5 wt %
Diethylene glycol	10 wt %
Surfynol TG	1 wt %
Pure water	Balance

Cyan ink 2	
C.I. Direct Blue 199	3 wt %
Diethylene glycol	10 wt %
Surfynol TG	1 wt %

-continued

Danfix 723 (reactant, resin component 35%, manufactured Nitto Boseki Co., Ltd.)	3 wt %
Potassium hydroxide	1 wt %
Pure water	Balance

Cyan ink 3

C.I. Pigment Blue 15:3	2 wt %
Styrene/acrylic copolymer ammonium salt (anionic dispersant)	1 wt %
Microgel E-5002	3.5 wt %
Sucrose	0.7 wt %
Maltitol	6.3 wt %
Glycerin	10 wt %
2-Pyrrolidone	2 wt %
Surfynol TG	1 wt %
Pure water	Balance

Cyan ink 4

C.I. Pigment Blue 15:3	2 wt %
Solsperse 27000 (nonionic dispersant, manufactured by Zeneca Co., Ltd.)	1 wt %
Magnesium acetate tetrahydrate (reactant)	5 wt %
Sucrose	0.7 wt %
Maltitol	6.3 wt %
Glycerin	10 wt %
2-Pyrrolidone	2 wt %
Surfynol 465	1 wt %
Ethanol	3 wt %
Pure water	Balance

Light-colored cyan ink 1

C.I. Pigment Blue 15:3	0.3 wt %
Solsperse 27000 (nonionic dispersant)	0.2 wt %
Diethylene glycol	10 wt %
Surfynol TG	1 wt %
Ammonium hydroxide	1 wt %
Magnesium sulfate tetrahydrate (reactant)	10 wt %
Pure water	Balance

Black ink 1

Carbon black Raven 1080 (manufactured by Columbian Carbon)	5 wt %
Styrene/acrylic acid copolymer ammonium salt (anionic dispersant)	1 wt %
Voncoat 4001 (acrylic resin emulsion, resin component 50%, MFT = 5° C., manufactured by Dainippon Ink and Chemicals, Inc.)	4 wt %
Sucrose	0.7 wt %
Maltitol	6.3 wt %
Glycerin	10 wt %
2-Pyrrolidone	2 wt %
Surfynol TG	1 wt %
Pure water	Balance

Black ink 2

Carbon black MA 7 (manufactured by Mitsubishi Kasei Corp.)	5 wt %
Solsperse 27000 (nonionic dispersant)	1 wt %
Glycerin	15 wt %
Surfynol TG	1 wt %
Dan fix 723 (reactant)	3 wt %
Potassium hydroxide	1 wt %
Pure water	Balance

Print Evaluation Test 1

Printing was carried out using ink sets 1 and 2 shown in the following table with ink jet printer MJ700V2C (manufactured by Seiko Epson Co., Ltd.) onto the following papers. In the printing, a solid image (100% duty) of a cyan ink, a magenta ink, or a yellow ink was printed, and, immediately after that, a letter was printed on the solid image using a black ink. In this case, simultaneous deposition of a yellow ink was always performed on a dot to which the black ink was to be deposited.

(1) Xerox P Paper (Xerox Corp.)

(2) Ricopy 6200 Paper (Ricoh Co. Ltd.)

(3) Xerox 4024 Paper (Xerox Corp.)

(4) Neenah Bond Paper (Kimberly-Clark)

(5) Xerox R Paper (Xerox Corp., recycled paper)

(6) Yamayuri (Honshu Paper Co., Ltd., recycled paper)

The letter with the black ink for each print was examined for uneven color mixing at its boundary areas. The results were evaluated according to the following criteria.

No color mixing with clear boundaries for all the test paper: excellent (A)

Color mixing in a feather form for any test paper: good (B)

Color mixing, for all the test papers, to such an extent that the outline of the letter is blurred: unacceptable (NG)

The results are summarized in the following table.

TABLE 1

	Ink	Reactant	Bleeding
Ink set 1	Yellow ink 1	Polyvalent metal salt	A
	Magenta ink 1	Polyvalent metal salt	A
	Cyan ink 3	—	A
	Black ink 1	—	—
Ink set 2	Yellow ink 3	—	A
	Magenta ink 3	—	A
	Cyan ink 2	Polyallylamine	A
	Black ink 2	Polyallylamine	—

Print Evaluation Test 2

Printing was carried out using ink sets 3, 4, 5, and 6 shown in the following table with ink jet printer MJ700V2C. A solid image (100% duty) of a cyan ink, a magenta ink, or a yellow ink was printed in the same papers as used in the print evaluation test 1. Further, immediately after that, a black letter was formed thereon by overprinting an cyan ink, a magenta ink, and a yellow ink. The black letter for each print was examined for uneven color mixing at its boundary areas. The results were evaluated according to the same criteria as used in the print evaluation test 1. The results are summarized in the following table.

TABLE 2

	Ink	Reactant	Bleed
Ink set 3	Yellow ink 1	Polyvalent metal salt	A
	Magenta ink 3	—	A
	Cyan ink 3	—	A
Ink set 4	Yellow ink 2	Polyallylamine	A
	Magenta ink 2	Polyallylamine	A
	Cyan ink 1	—	A
Ink set 5	Yellow ink 3	—	B
	Magenta ink 2	Polyallylamine	A
	Cyan ink 2	Polyallylamine	A
Ink set 6	Yellow ink 3	—	B
	Magenta ink 3	—	A
	Cyan ink 2	Polyallylamine	A

Print Evaluation Test 3

Printing was carried out using an ink set 7 shown in the following table with ink Jet printer MJ700V2C in the same

manner as in the print evaluation test 1, except that a solid image of magenta was formed by overprinting a light-colored magenta ink and a magenta ink, a solid image of cyan was formed by overprinting a light-colored cyan ink and a cyan ink. Further, simultaneous deposition of a light-colored magenta ink was always performed on a dot to which the black ink was to be deposited. For each print, the letter formed using the black ink composition was examined for uneven color mixing at its boundary areas. The results were evaluated according to the same criteria as used in the print evaluation test 1. The results are summarized in the following table.

TABLE 3

	Ink	Reactant	Bleeding
Ink set 7	Light-colored magenta ink 1	Polyvalent metal salt	A
	Light-colored cyan ink 1	Polyvalent metal salt	A
	Yellow ink 3	—	A
	Magenta ink 3	—	A
	Cyan ink 3	—	A
	Black ink 1	—	—

Print Evaluation Test 4

Printing was carried out using an ink set 8 shown in the following table with ink jet printer MJ700V2C in the same manner as in the print evaluation test 1, except that a solid image of magenta was formed by overprinting a light-colored magenta ink and a magenta ink and a blotted image of cyan was formed by overprinting a light-colored cyan ink and a cyan ink. Further, deposition of a yellow ink was not performed on a dot to which the black ink was to be deposited. For each print, the letter formed using the black ink composition was examined for uneven color mixing at its boundary areas. The results were evaluated according to the same criteria as used in the print evaluation test 1. The results are summarized in the following table.

TABLE 4

	Ink	Reactant	Bleeding
Ink set 8	Light-colored magenta ink 1	Polyvalent metal salt	A
	Light-colored cyan ink 1	Polyvalent metal salt	A
	Yellow ink 1	Polyvalent metal salt	A
	Magenta ink 3	—	A
	Cyan ink 3	—	A
	Black ink 1	—	—

Print Evaluation Test 5

An ink set 9 specified in the following table was evaluated in the same manner as in the print evaluation test 1. The results are summarized in the following table.

TABLE 5

	Ink	Reactant	Bleeding
Ink set 9	Yellow ink 1	Polyvalent metal salt	A
	Magenta ink 1	Polyvalent metal salt	A
	Cyan ink 4	Polyvalent metal salt	A
	Black ink 1	—	—

Test on Storage Stability of Inks

The ink compositions prepared above were placed in respective sample bottles, and the bottles were hermetically sealed and stored under an environment of 50° C. Three months after the initiation of the storage, the viscosity, the surface tension and PH of the inks were measured and found to be substantially the same as those before the storage.

What is claimed is:

1. An ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition containing a magenta colorant, and a cyan ink composition containing a cyan colorant,

the magenta ink composition and the cyan ink composition each comprising a resin emulsion, an inorganic oxide colloid or both,

the yellow ink composition comprising a reactant which breaks the state of dispersion or dissolution of the colorant and the resin emulsion in the magenta ink composition and the cyan ink composition.

2. The ink set according to claim **1**, which further comprises a black ink composition.

3. The ink set according to claim **2**, wherein the black ink composition comprises a resin emulsion, an inorganic oxide colloid or both and the reactant can break the state of dispersion or dissolution of the colorant and the resin emulsion, the inorganic oxide colloid or both in the black ink composition.

4. The ink set according to claim **1**, wherein the ink composition which comprises the reactant comprises a non-ionic dispersant.

5. The ink set according to claim **4**, wherein the ink composition which is free form the reactant comprises an anionic dispersant.

6. The ink set according to claim **1**, wherein the colorant is a pigment and the reactant is a polyvalent metal salt or a polyallylamine or a derivative thereof.

7. A recording method comprising the step of: depositing an ink composition onto a recording medium to conduct printing,

wherein an ink composition in the ink set according to claim **1** is used as the ink composition.

8. The recording method according to claim **7**, wherein the mass of the droplets of the ink compositions which comprise the reactant are less than 30 to 100% by weight of the mass of the droplets of the ink compositions which are free from the reactant.

9. A record produced by the recording method according to claim **7**.

10. An ink jet recording method comprising the step of: ejecting and depositing droplets of an ink composition onto a recording medium to conduct printing,

wherein an ink composition in the ink set according to claim **1** is used as the ink composition.

11. The ink jet recording method according to claim **10**, wherein the mass of the droplets of the ink compositions ejected are such that a pixel formed by the ink composition which comprises the reactant is smaller than a pixel formed by the ink composition which is free from the reactant.

12. An ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition containing a magenta colorant, and a cyan ink composition containing a cyan colorant,

the cyan ink composition comprising a resin emulsion, an inorganic oxide colloid or both,

the yellow ink composition and the magenta ink composition each comprising a reactant which breaks the state

of dispersion or dissolution of the colorant and the resin emulsion in the cyan ink composition.

13. An ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition having a lower color density containing a magenta colorant, a magenta ink composition having a higher color density containing a magenta colorant, a cyan ink composition having a lower color density containing a cyan colorant, and a cyan ink composition having a higher color density containing a cyan colorant,

the magenta ink composition having a lower color density, and the cyan ink composition having a lower color density each comprising a reactant which breaks the state of dispersion or dissolution of the colorant in the yellow ink composition, the magenta ink composition having a higher color density and the cyan ink composition having a higher color density.

14. The ink set according to claim **13**, wherein the yellow ink composition, the magenta ink composition having a higher color density and the cyan ink composition having a higher color density each comprising a resin emulsion, an inorganic oxide colloid or both, the reactant breaking the state of dispersion or dissolution of the resin emulsion, the inorganic oxide colloid or both.

15. An ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition having a lower color density containing a magenta colorant, a magenta ink composition having a higher color density containing a magenta colorant, a cyan ink composition having a lower color density containing a cyan colorant, and a cyan ink composition having a higher color density containing a cyan colorant,

the yellow ink composition, the magenta ink composition having a lower color density, and the cyan ink composition having a lower color density each comprising a reactant which breaks the state of dispersion or dissolution of the colorant in the magenta ink composition having a higher color density and the cyan ink composition having a higher color density.

16. The ink set according to claim **15**, wherein the magenta ink composition having a higher color density and the cyan ink composition having a higher color density each comprising a resin emulsion, an inorganic oxide colloid or both, the reactant breaking the state of dispersion or dissolution of the resin emulsion, and/or the inorganic oxide colloid.

17. An ink set comprising a yellow ink composition containing a yellow colorant, a magenta ink composition containing a magenta colorant, a cyan ink composition containing a cyan colorant, and a black ink composition containing a black colorant,

the black ink composition comprising a resin emulsion, an inorganic oxide colloid or both,

the yellow ink composition, the magenta ink composition, and cyan ink composition each comprising a reactant which breaks the state of dispersion or dissolution of the colorant and the resin emulsion in the black ink composition.

* * * * *

US006482256B1

EXHIBIT B

(12) **United States Patent**
Kanaya et al.

(10) **Patent No.: US 6,482,256 B1**
(45) **Date of Patent: Nov. 19, 2002**

(54) **INK SETS**

(75) Inventors: **Miharu Kanaya**, Nagano-ken (JP); **Jun Ito**, Nagano-ken (JP); **Hiroshi Fukumoto**, Nagano-ken (JP)

(73) Assignee: **Seiko Epson Corporation**, Tokyo (JP)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

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(52) **U.S. Cl.** **106/31.51**; 106/31.47; 106/31.48; 106/31.49; 106/31.52
(58) **Field of Search** 106/31.51, 31.47, 106/31.48, 31.49, 31.52

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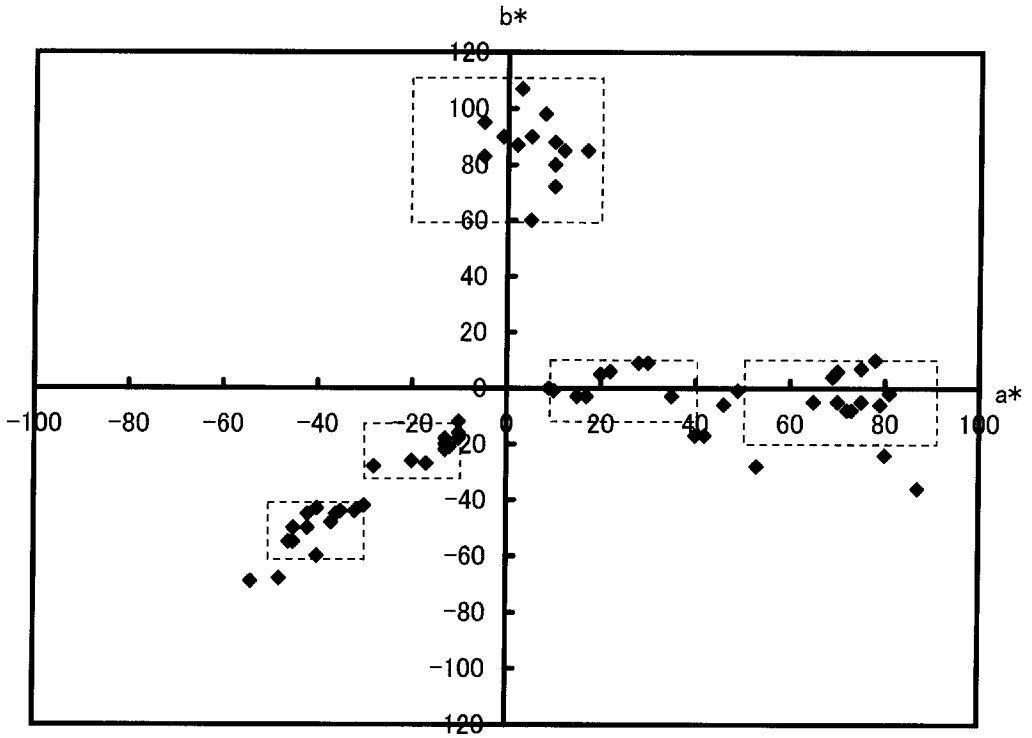
Primary Examiner—Helene Klemanski
(74) *Attorney, Agent, or Firm*—Ladas & Parry

(57) **ABSTRACT**

An ink set is provided which can realize images having excellent lightfastness and color reproduction. The ink set comprises magenta ink compositions, the magenta ink compositions containing specific compounds as colorants.

28 Claims, 1 Drawing Sheet



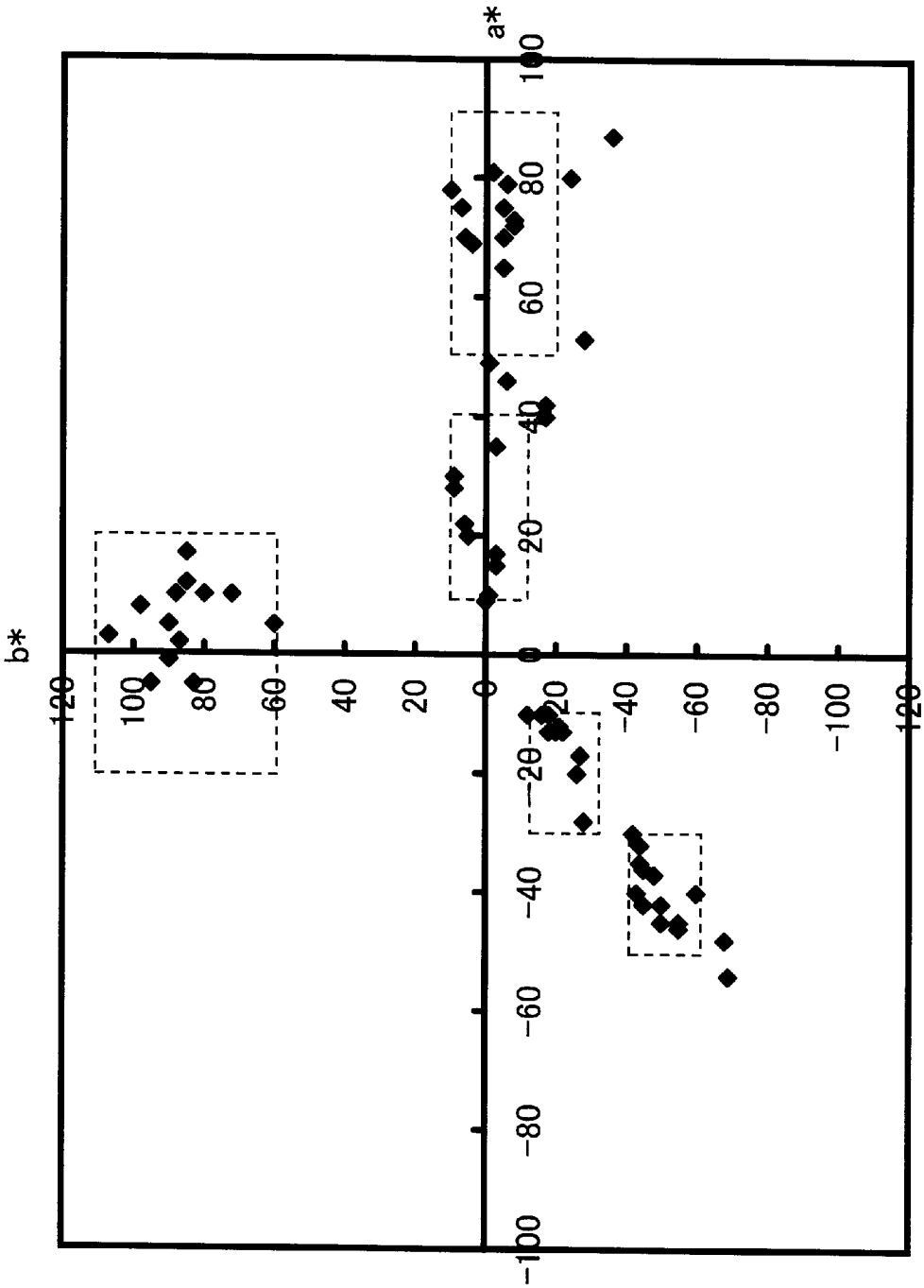


Fig.1

INK SETS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to color ink sets having excellent color reproduction and lightfastness.

2. Background Art

In general, images produced by ink compositions, when exposed to indoor or outdoor light beams, the open air and the like for a long period of time, are frequently deteriorated due to an influence of ultraviolet light, visible light, various gases contained in the air or the like. In particular, in the case of color images produced by a plurality of ink compositions, the presence of even one color ink composition having poor lightfastness causes a change in hue of images, resulting in extremely deteriorated quality of color images. This has led to a demand for ink compositions capable of yielding highly weathering-resistant images which, even when stored for a long period of time, are less likely to be deteriorated.

Further, in recent years, attention has been drawn to ink jet recording. The ink jet recording is a printing method wherein droplets of an ink composition are ejected and deposited onto recording media, such as paper, to conduct printing. This method has a feature that images having high resolution and high quality can be printed at a high speed by means of relatively inexpensive apparatuses. Ink jet recording apparatuses utilizing this method are commercially widely accepted by virtue of good print quality, low cost, relatively quiet operation, and graphics-forming capability. Among others, thermal (bubble jet) and piezoelectric drop-on-demand printers have been very successful on the market, and have been widely used as printers for personal computers for office and domestic applications.

In recent years, a method has become used wherein a plurality of color ink compositions are provided and used in the formation of color images by ink jet recording. In general, color images are formed using three colors of a yellow ink composition, a magenta ink composition, and a cyan ink composition, and optionally four colors of the above three color compositions plus a black ink composition. In some cases, six colors of the above four colors plus a light cyan ink composition and a light magenta ink composition are used in the formation of color images. What is required of ink compositions for the formation of such color images is that they as such can exhibit good color development and, in addition, when used in combination with a plurality of ink compositions, can develop good intermediate colors.

Further, ink compositions constituting ink sets used in this ink jet recording are required to have properties such that they have suitable property values, such as proper viscosity and surface tension values, have high optical density, can yield sharp color tone and images, can yield images having excellent fastness properties, such as excellent waterfastness and lightfastness, have excellent storage stability, are less likely to cause nozzle clogging, and are free from problems associated with an odor and safety. In order to satisfy a large part of these property requirements, water-base inks prepared by dissolving water-soluble dyes in water or in a mixed solution of water and a water-soluble organic solvent are used. At that time, ink compositions having various hues are prepared from dyes having various hues.

Various image properties, such as color tone, lightfastness, and waterfastness, are greatly influenced by the properties of colorants in the ink compositions, and various dyes have hitherto been studied in the art.

SUMMARY OF THE INVENTION

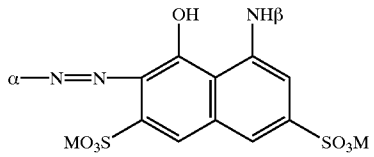
The present inventors have now found that ink sets comprising a combination of specific color ink compositions can realize images having excellent color reproduction and, at the same time, having excellent lightfastness. The present invention has been made based on such finding.

Accordingly, it is an object of the present invention to provide an ink set which can realize images having excellent lightfastness and color reproduction.

Thus, according to one aspect of the present invention, there is provided a magenta ink set comprising two magenta ink compositions different from each other in color density, a magenta ink composition with higher color density and a magenta ink composition with lower color density,

said magenta ink composition with higher color density containing as a colorant a compound represented by formula (III)

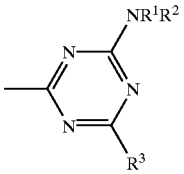
(III)



wherein

α represents a C_1–C_4 alkyl or alkoxy group or an OH—, SO_3H—, or COOM-substituted phenyl or naphthyl group;

β represents a hydrogen atom or a group represented by formula



wherein

R^1represents a hydrogen atom or an OH— or COOH-substituted C_1–C_4 alkyl group,

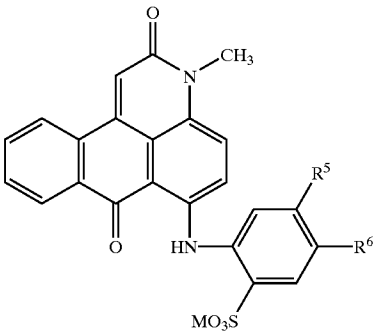
R^2 represents an OH—, OCH_3—, OC_2H_5—, SO_3M—, or COOM-substituted C_1–C_4 alkyl or phenyl group, and

R^3 represents an OH, COOH, or NHR^4 wherein R^4 represents an SO_3M— or COOH-substituted C_1–C_4 alkyl group; and

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine,

said magenta ink composition with lower color density containing as a colorant a compound represented by formula (IV):

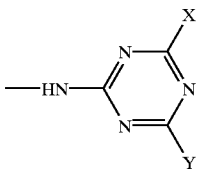
(IV)



wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine;

R^5 represents a hydrogen atom, a chlorine atom or a group represented by formula



wherein

X represents an anilino group substituted by at least one SO_3M and

Y represents OH, a chlorine atom, or a morpholino group; and

R^6 represents a hydrogen atom, a chlorine atom, SO_3M, or a C_1–C_4 alkyl group.

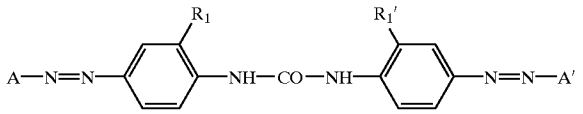
According to another aspect of the present invention, there is provided a magenta ink composition comprising as a colorant the compound represented by formula (III) and the compound represented by formula (IV) in a weight ratio of 1:1 to 1:5. Further, according to the present invention, there is provided an ink set comprising this magenta ink composition.

According to a further aspect of the present invention, there is provided an ink set comprising: a yellow ink composition; two magenta ink compositions different from each other in color density, a magenta ink composition with higher color density and a magenta ink composition with lower color density; and two cyan ink compositions different from each other in color density, a cyan ink composition with higher color density and a cyan ink composition with lower color density, said ink compositions containing as colorants the following respective specific compounds.

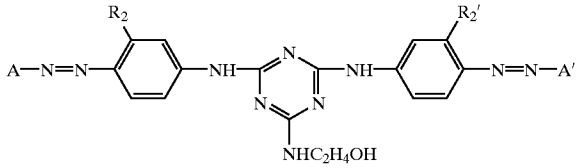
Specifically, the ink set according to this aspect of the present invention comprises: a yellow ink composition; two magenta ink compositions different from each other in color density, a magenta ink composition with higher color density and a magenta ink composition with lower color density; and two cyan ink compositions different from each other in color density, a cyan ink composition with higher color density and a cyan ink composition with lower color density,

said yellow ink composition containing as a colorant a compound represented by formula (I) and/or a compound represented by formula (II):

(I)



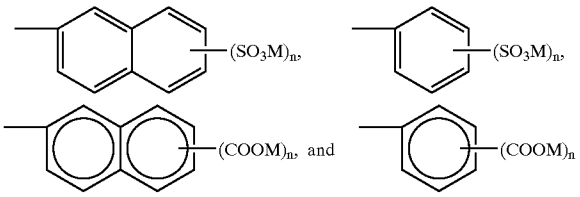
(II)



wherein

R_1, R_1', R_2, and R_2' each independently represent CH_3 or OCH_3; and

A and A' each independently represent a group having a structure selected from the group consisting of



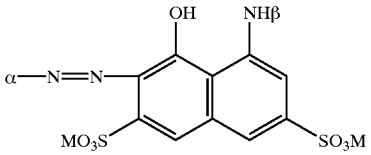
wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine; and

n is an integer of 1 or 2,

said magenta ink composition with higher color density containing as a colorant a compound represented by formula (III):

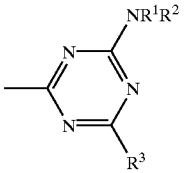
(III)



wherein

α represents a C_1–C_4 alkyl or alkoxy group or an OH—, SO_3H—, or COOM-substituted phenyl or naphthyl group;

β represents a hydrogen atom or a group represented by formula



wherein

R^1 represents a hydrogen atom or an OH— or COOH-substituted C_1–C_4 alkyl group,

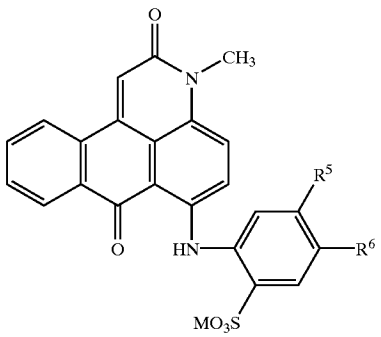
R^2 represents an OH—, OCH_3—, OC2H,—, SO_3M—, or COOM-substituted C_1–C_4 alkyl or phenyl group, and

R^3 represents an OH, COOH, or NHR^4 wherein R^4 represents an SO_3M— or COOH-substituted C_1–C_4 alkyl group; and

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine,

and/or a compound represented by formula (IV):

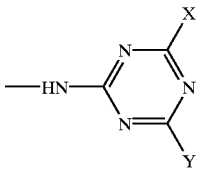
(IV)



wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine;

R^5 represents a hydrogen atom, a chlorine atom or a group represented by formula



wherein

X represents an anilino group substituted by at least one SO_3M and

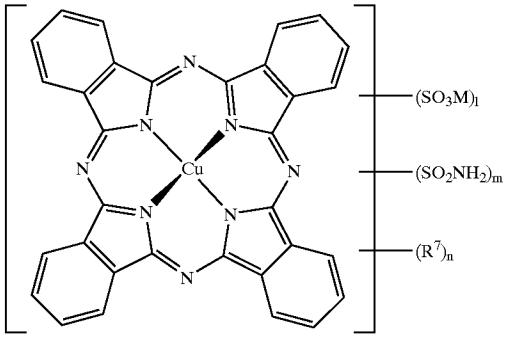
Y represents OH, a chlorine atom, or a morpholino group; and

R^6 represents a hydrogen atom, a chlorine atom, SO_3M, or a C_1–C_4 alkyl group,

said magenta ink composition with lower color density containing as a colorant the compound represented by formula (III) and/or the compound represented by formula (IV),

said cyan ink composition with higher color density and said cyan ink composition with lower color density each containing as a colorant a compound represented by formula (V):

(V)



wherein

R^7 represents OH, COOM, or R^8COOM wherein R^8 represents a C_4–C_9 alkyl group; and

1, m, and n are each 0 to 4 with (1+m+n)=4.

According to the ink sets of the present invention, the presence of specific compounds as the colorant in the respective ink compositions can significantly improve the color reproduction of printed images and, at the same time, can yield images having improved lightfastness. Further, according to the ink sets of the present invention, nozzle clogging of a recording head can be prevented to realize stable ink ejection.

BRIEF DESCRIPTION OF THE DRAWING

FIG. **1** is a diagram showing the results of a color reproduction test in an evaluation test E, that is, showing the distribution of hues of inks determined by calculation of color with a spectrophotometer, wherein distribution points of hue correspond to data shown in Table 23.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Ink Set

The ink set according to the present invention may be used in recording methods using an ink composition. Recording methods using an ink composition include, for example, an ink jet recording method, a recording method using writing utensils, such as pens, and other various recording methods. Preferably, the ink composition according to the present invention is used in the ink jet recording method.

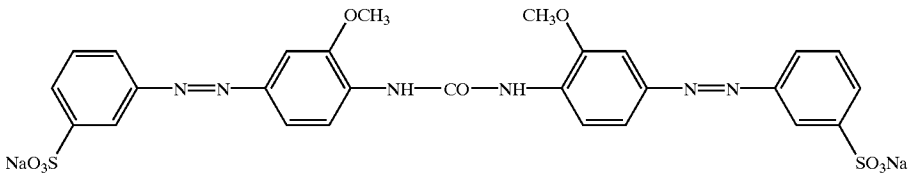
The ink set according to one aspect of the present invention basically comprises two magenta ink compositions different from each other in color density. The ink set according to another aspect of the present invention comprises a yellow ink composition, two magenta ink compositions different from each other in color density, and two cyan ink compositions different from each other in color density. Alternatively, the ink set may comprise a yellow ink composition, a magenta ink composition with a single color density, and a cyan ink composition with a single color density. The two ink compositions different from each other in color density may be divided into an ink composition with higher color density and an ink composition with lower color density.

Yellow Ink Composition

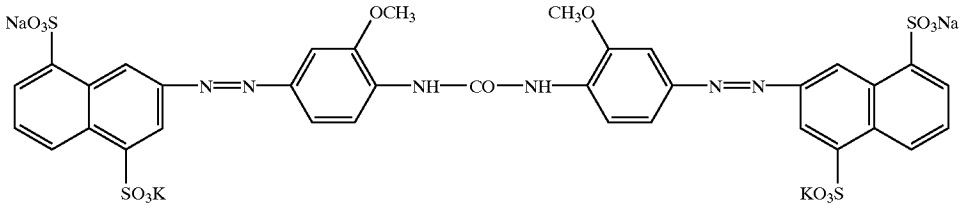
The yellow ink composition to be used in the present invention contains as a colorant a compound represented by formula (I) and/or a compound represented by formula (II). According to the present invention, compounds represented by formula (I) and/or compounds represented by formula (II) as the colorant may be used alone or as a mixture of two or more.

Compounds represented by formula (I) and/or compounds represented by formula (II) include C.I. Direct Yellow 86 and C.I. Direct Yellow 132. Further, the following compounds may be mentioned as specific examples thereof.

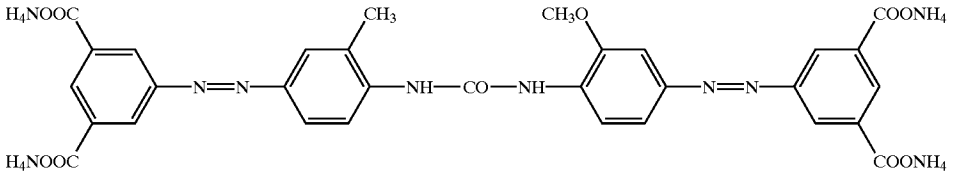
(Y-1)



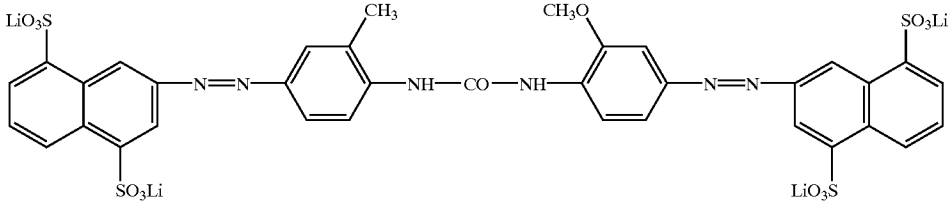
(Y-2)



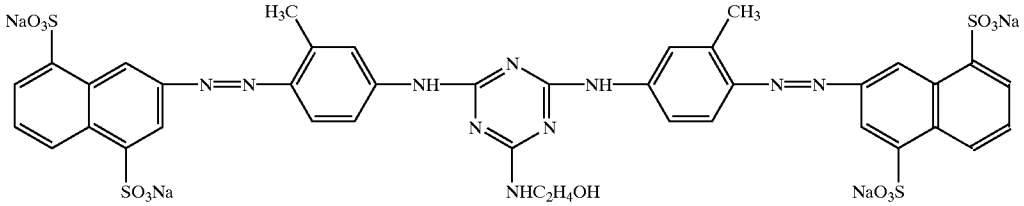
(Y-3)



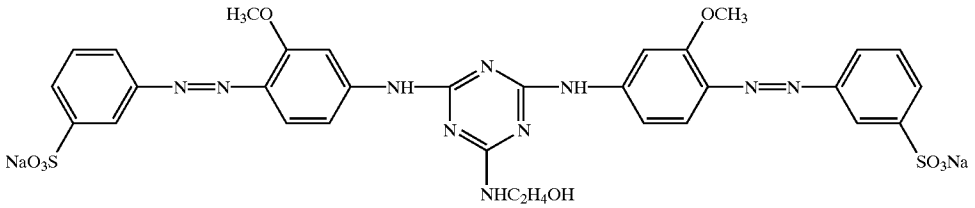
(Y-4)



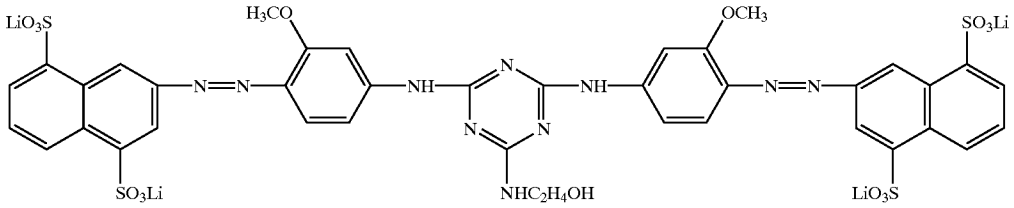
(Y-5)



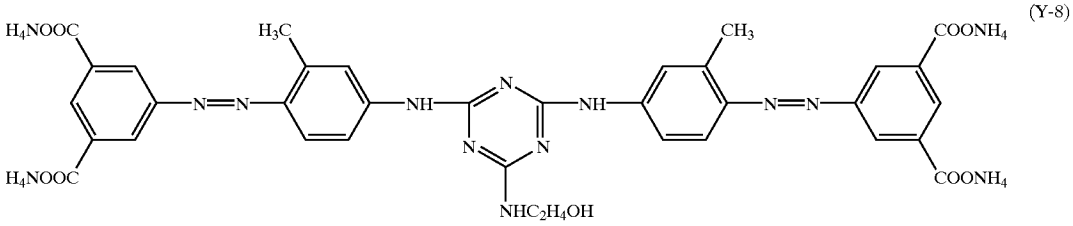
(Y-6)



(Y-7)



-continued



(Y-8)

The concentration of the colorant in the yellow ink composition may be suitably selected. In general, however, the ink composition preferably contains 0.3 to 6.0% by weight in total of the compound represented by formula (I) and/or the compound represented by (II). This concentration range is preferred also from the viewpoint of the balance between the magenta ink composition and the cyan ink composition. Further, when the formation of blotted images (solid printing with 100% duty) on the so-called "plain papers" is carried out, the OD value of yellow is preferably in the range of 1.0 to 1.5. Therefore, the content of the compound represented by formula (I) and/or the compound represented by formula (II) in the yellow ink composition is preferably 0.3 to 4.0% by weight in total, still more preferably 1.5 to 4.0% by weight in total.

Magenta Ink Compositions

The two magenta ink compositions different from each other in color density to be used in the ink set according to the present invention are composed of a magenta ink composition with higher color density (hereinafter often referred to as "deep magenta ink") and a magenta ink composition with lower color density (hereinafter often referred to as "light magenta ink"). Ink jet recording using a deep magenta ink and a light magenta ink can provide recorded images having high sharpness and excellent lightfastness and gas resistance.

According to one aspect of the present invention, there is provided a magenta ink set comprising: a magenta ink composition with higher color density containing as a colorant the compound represented by formula (III) as defined above; and a magenta ink composition with lower color density containing as a colorant the compound represent by formula (IV) as defined above.

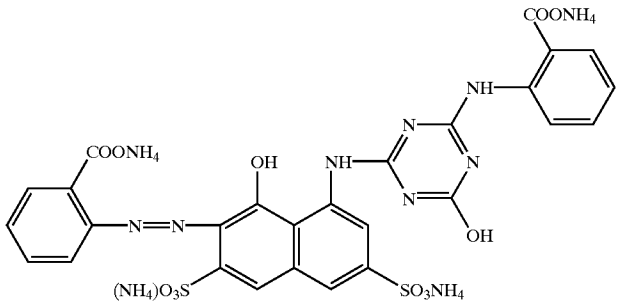
According to another aspect of the present invention, there is provided a magenta ink composition comprising the compound represented by formula (III) and the compound represented by formula (IV) as a colorant in a weight ratio of 1:1 to 1:5. At that time, the content of the colorant is preferably 0.5 to 5% by weight based on the total amount of the ink composition. According to a further aspect of the present invention, there is provided a magenta ink set comprising this magenta ink composition.

Ink compositions used in combination with the magenta ink set according to the present invention are not particularly limited. Specifically, the magenta ink set may be used in combination with desired yellow ink compositions, cyan ink compositions, and, if necessary, black ink compositions. The magenta ink compositions constituting the magenta ink set may be identical to the above magenta ink compositions in chemical composition and the like except for use in combination with the above ink compositions. The magenta ink set according to the present invention can realize highly lightfast and sharp images.

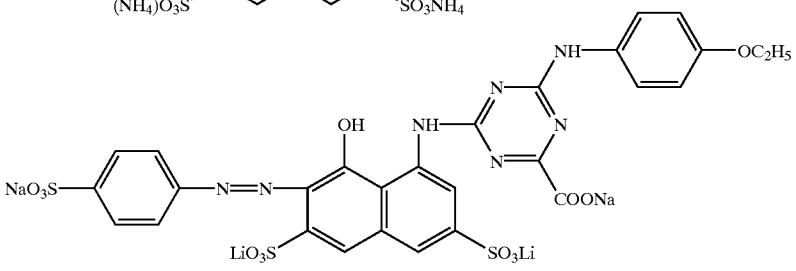
The magenta ink composition with higher color density to be used in the present invention contains as a colorant the compound represented by formula (III) and/or the compound represented by formula (IV). The ink composition containing this compound as such, that is, when used in the formation of a single-color image, can yield images having excellent sharpness and lightfastness.

Specific examples of compounds represented by formula (III) include the following compounds.

(M-1)

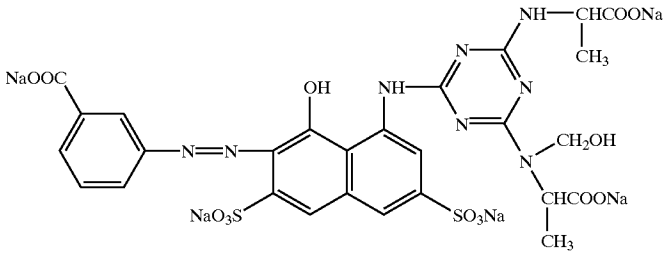


(M-2)

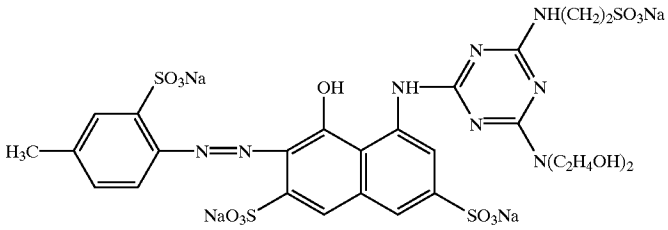


-continued

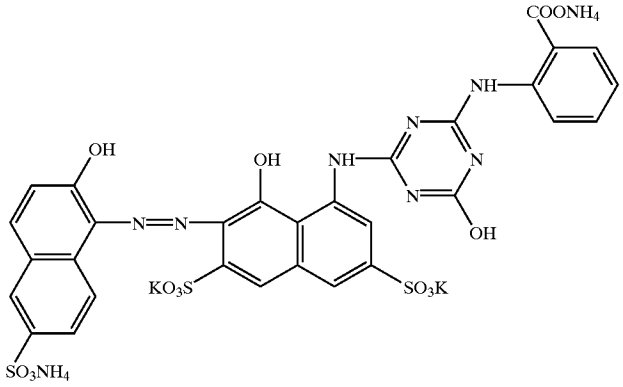
(M-3)



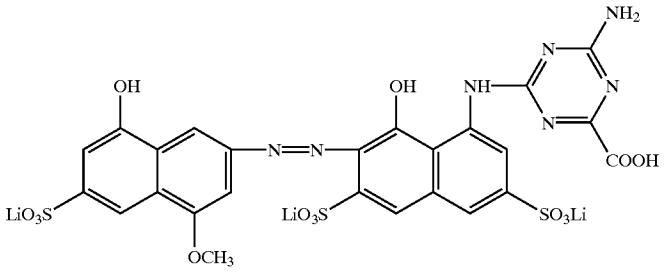
(M-4)



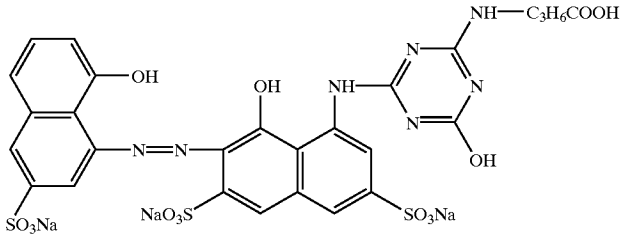
(M-5)



(M-6)

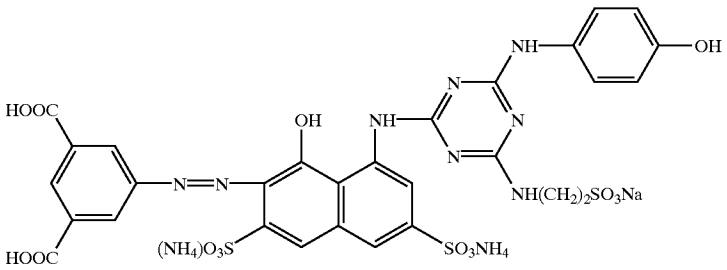


(M-7)

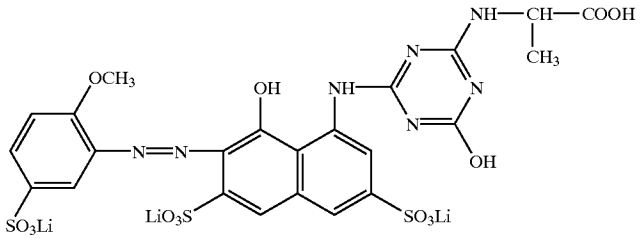


-continued

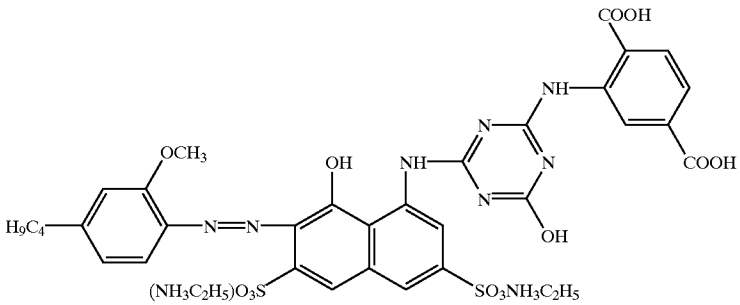
(M-8)



(M-9)

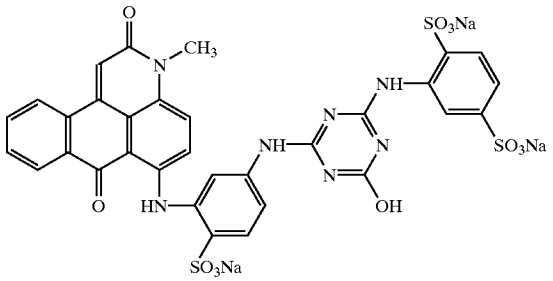


(M-10)

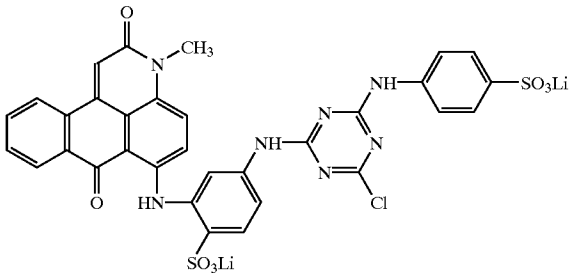


Specific examples of compounds represented by formula (IV) include the following compounds.

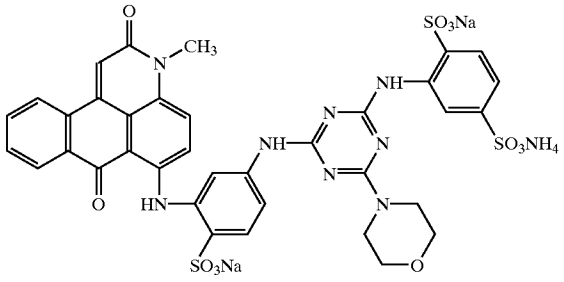
(LM-1)



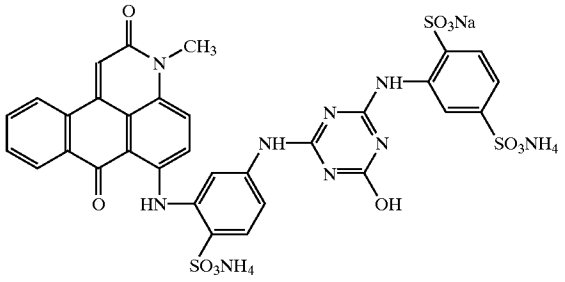
(LM-2)



(LM-3)

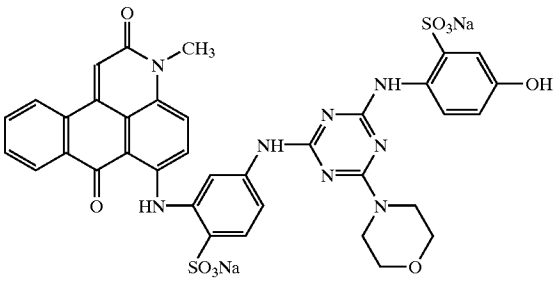


(LM-4)

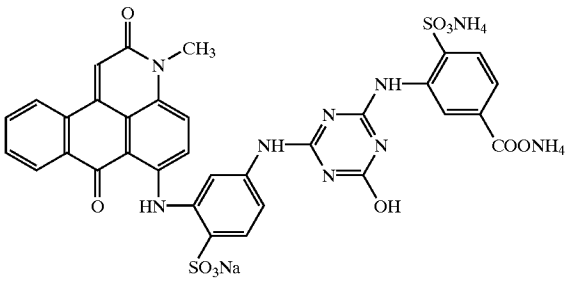


-continued

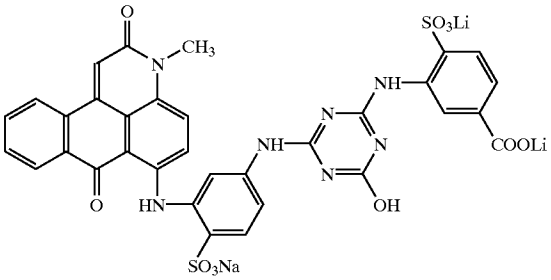
(LM-5)



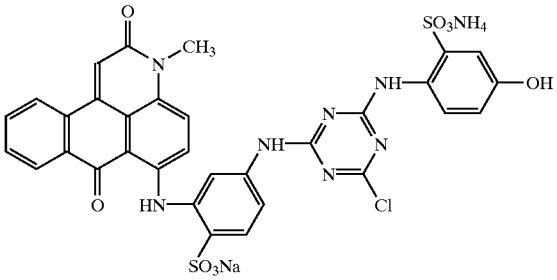
(LM-6)



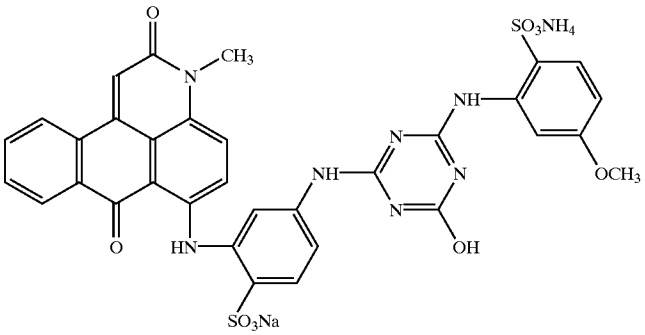
(LM-7)



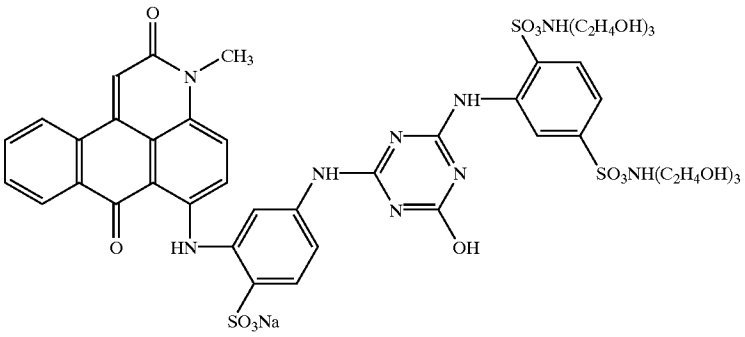
(LM-8)



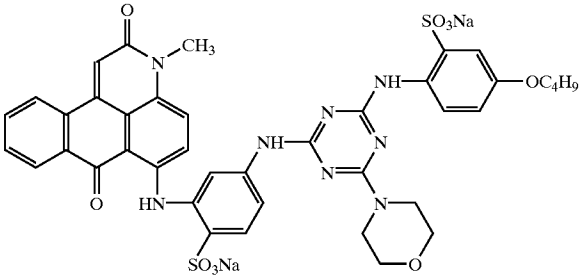
(LM-9)



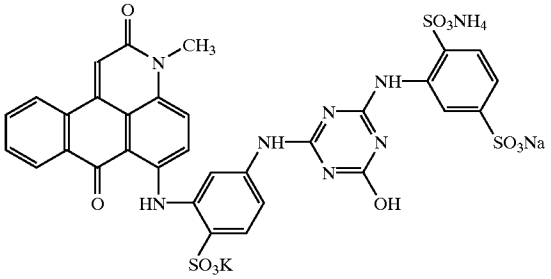
(LM-10)



(LM-11)

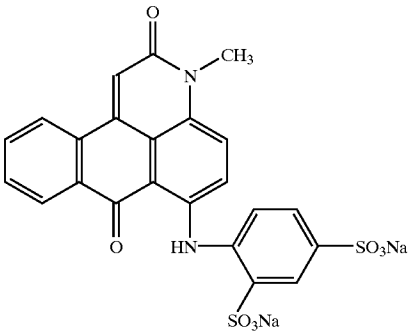


(LM-12)

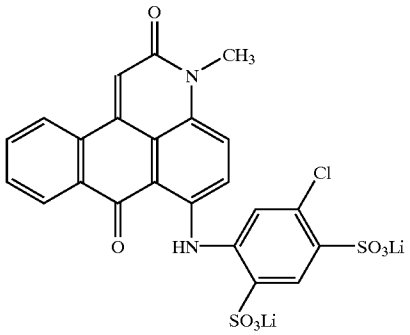


-continued

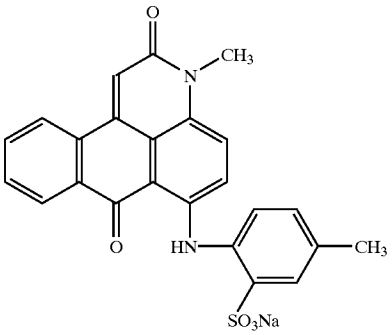
(LM-13)



(LM-14)



(LM-15)



According to the present invention, compounds represented by formula (III) and/or compounds represented by formula (IV) may be used alone or as a mixture of two or more, as the colorant used in the magenta ink composition with higher color density.

According to one preferred embodiment of the present invention, the compound represented by formula (III) is preferred as the colorant used in the magenta ink composition with higher color density.

The concentration of the colorant in the magenta ink composition with higher color density may be properly selected. In general, however, the ink composition preferably contains the compound represented by formula (III) in an amount of 1.0 to 5.0% by weight. Further, when the formation of blotted images (solid printing with 100% duty) on the so-called "plain papers" is carried out, the OD value of magenta is preferably in the range of 1.0 to 1.5. Therefore, the content of the compound represented by formula (III) in the magenta ink composition with higher color density is more preferably 1.0 to 4.0% by weight, still more preferably 1.5 to 3.5% by weight.

The magenta ink composition with lower color density used in the present invention contains as the colorant the compound represented by formula (III) and/or the compound represented by formula (IV).

The compound represented by formula (III) and the compound represented by formula (IV) may be selected from the compounds as used in the magenta ink composition with higher color density.

According to the present invention, compounds represented by formula (III) and/or compounds represented by formula (IV) may be used alone or as a mixture of two or more, as the colorant used in the magenta ink composition with lower color density.

According to one preferred embodiment of the present invention, the compound represented by formula (IV) is preferred as the colorant used in the magenta ink composition with lower color density.

The concentration of the colorant in the magenta ink composition with lower color density may be properly selected according to the color balance between the magenta ink composition with lower color density and the magenta ink composition with higher color density used in combination with the magenta ink composition with lower color density. In general, however, when the compound represented by formula (IV) is used in the magenta ink composition with lower color density, the content of the compound represented by formula (IV) in the magenta ink composition with lower color density is preferably 0.5 to 3.0% by weight, more preferably 1 to 3% by weight. When the compound falls within the above concentration range, the magenta ink composition with lower color density, when used in combination with the magenta ink composition with higher color density, can offer a good color balance.

When a mixture of the compound represented by formula (III) with the compound represented by formula (IV) is used as the colorant, the weight ratio of the compound represented by formula (III) and the compound represented by formula (IV) is preferably in a weight ratio of 1:1 to 1:5.

Cyan Ink Composition

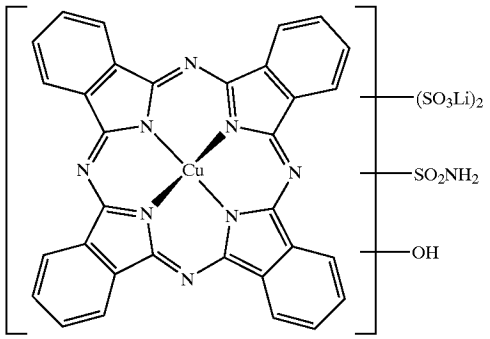
The two cyan ink compositions different from each other in color density to be used in the ink set according to the present invention are composed of a cyan ink composition with higher color density (hereinafter often referred to as "deep cyan ink") and a cyan ink composition with lower color density (hereinafter often referred to as "light cyan ink").

The cyan ink composition with higher color density and the cyan ink composition with lower color density to be used in the present invention each contain as the colorant the compound represented by formula (V).

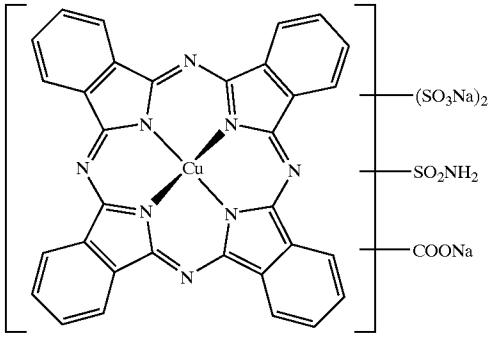
The difference in color density between the ink compositions different from each other in color density may be provided by using two ink compositions having different dye concentrations, or by properly selecting the types of colorants used.

Specific examples of compounds represented by formula (V) include those represented by the following formulae, C.I. Direct Blue 86, 87, and 199, and Projet Fast Cyan 2 (products of Zeneca).

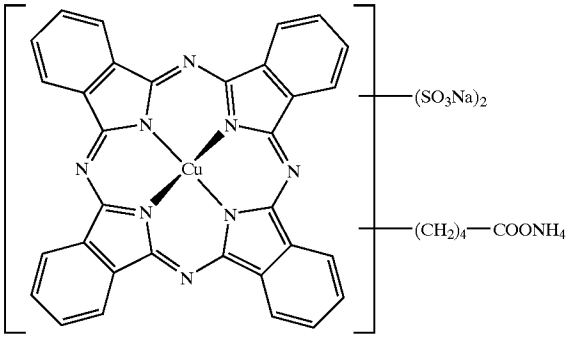
(C-1)



(C-2)



(C-3)



Regarding the colorant to be used in the cyan ink composition with higher color density and the colorant to be used in the cyan ink composition with lower color density according to the present invention, compounds represented by formula (V) may be used alone or as a mixture of two or more.

The concentration of the colorant in the cyan ink composition with higher color density may be properly selected. In general, however, the cyan ink composition with higher color density preferably contains 2.0 to 6.0% by weight of the compound represented by formula (V). Further, when the formation of blotted images (solid printing with 100% duty) on the so-called "plain papers" is carried out, the OD value of cyan is preferably in the range of 1.0 to 1.5. Therefore, the content of the compound represented by formula (V) in the cyan ink composition with higher color density is more preferably 2.5 to 4.5% by weight.

The concentration of the colorant in the cyan ink composition with lower color density may be properly selected according to the color balance between the compound represented by formula (V) used as the colorant and the deep cyan ink used in combination with the light cyan ink. In general, preferably, the cyan ink composition with lower color density contains 0.4 to 1.5% by weight of the compound represented by formula (V).

When the cyan ink composition with lower color density contains the colorant in the above concentration range, the cyan ink composition with lower color density, when used in combination with the cyan ink composition with higher color density, can offer a good color balance.

According to one preferred embodiment of the present invention, in the ink set, the yellow ink composition contains 0.3 to 4.0% by weight in total of the compound represented by formula (I) and/or the compound represented by formula (II), the magenta ink composition with higher color density contains 1.0 to 4.0% by weight of the compound represented by formula (III), the magenta ink composition with lower color density contains 0.5 to 3.0% by weight of the compound represented by formula (IV), and, in this case, the cyan ink composition with higher color density contains 1.0 to 4.0% by weight of the compound represented by formula (V) and the cyan ink composition with lower color density contains 0.5 to 3.0% by weight of the compound represented by formula (V).

According to a further aspect of the present invention, there is provided an ink set comprising a yellow ink composition, a magenta ink composition, and a cyan ink composition, wherein the cyan ink composition contains as a colorant the compound represented by formula (V). The compound represented by formula (V) may be selected from the compounds as described above. The concentration of the colorant in the cyan ink composition may be properly selected. In general, however, the cyan ink composition preferably contains 1.0 to 4.0% by weight of the colorant.

In the ink set according to the present invention, the hue (a*, b*) of each ink composition constituting the ink set preferably falls within a specific range. In this case, the hue of the ink composition refers to hue as determined using spectral properties of a solution prepared by diluting 1 g of the ink composition with 1,000 ml of pure water. For example, measurement may be carried out with a spectrophotometer (U-3300, manufactured by Hitachi, Ltd.) under specific conditions (standard light source: D65, field of view: 2 degrees, measurement wavelength 300 to 800 nm), followed by color calculation to determinehue (L*, a*, b*). In this case, L*represents lightness, and a* and b* each represent hue (chromaticity). More specifically, a* represents the direction of red, −a* represents the direction of green, b* represents the direction of yellow, and −b* represents the direction of blue.

According to the present invention, when the ink set comprises a yellow ink composition, two magenta ink compositions different from each other in color density, and two cyan ink compositions different from each other in color density, the hue (a*, b*) is preferably in the range of (−20 to 20, 60 to 110) for the yellow ink composition, in the range of (50 to 90, −20 to 10) for the magenta ink composition with higher color density, in the range of (10 to 40, −10 to 10) for the magenta ink composition with lower color density, in the range of (−50 to −30, −60 to −40) for the cyan ink composition with higher color density, and in the range of (−30 to −10, −30 to −10) for the cyan ink composition with lower color density.

When the ink set according to the present invention comprises a yellow ink composition, a magenta ink composition with a single color density, and a cyan ink compo-

sition with a single color density, the hue (a*, b*) is preferably in the range of (−20 to 20, 60 to 110) for the yellow ink composition, in the range of (50 to 90, −20 to 10) for the magenta ink composition, and in the range of (−50 to −30, −60 to −40) for the cyan ink composition.

When the hues (a*, b*) of the ink compositions contained in the ink set fall within the respective ranges as described above, color images having excellent color reproduction and color tone can be provided.

Black Ink Composition

According to the present invention, the ink set comprising a yellow ink composition, two magenta ink compositions different from each other in color density, and two cyan ink compositions different from each other in color density may further comprise a black ink composition.

Any dye or pigment capable of yielding a black print may be used as a colorant contained in the black ink composition usable in the present invention. Such dyes include, for example, various dyes commonly used in ink compositions, especially used in ink jet recording, such as direct dyes, acid dyes, foodstuff dyes, basic dyes, reactive dyes, disperse dyes, vat dyes, soluble vat dyes, and reactive disperse dyes. Examples of pigments usable herein include black pigments such as carbon black.

The black ink composition usable in the present invention is preferably a water-soluble black ink from the viewpoint of safety and the like.

According to the present invention, these colorants may be contained, either alone or as a mixture of two or more, in the black ink composition.

Water, Water-soluble Organic Solvent, and Other Optional Ingredients

In the ink compositions to be used in the present invention, water or a mixed solution composed of water and a water-soluble organic solvent is suitable as a main solvent. Water may be pure water obtained, for example, by ion exchange, ultrafiltration, reverse osmosis, distillation or the like, or ultrapure water. Further, water, which has been sterilized by ultraviolet irradiation or by addition of hydrogen peroxide, is suitable because, when the ink composition is stored for a long period of time, it can prevent the growth of mold or bacteria.

In the ink compositions to be used in the present invention, when water is used as the main solvent, the water content is preferably 50 to 90% by weight, more preferably 60 to 80% by weight, based on the ink composition.

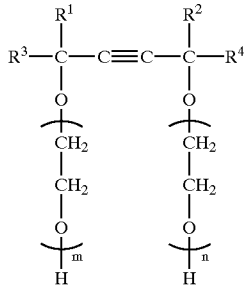
According to a preferred embodiment of the present invention, the solvent in the ink compositions to be used in the present invention is a mixed solution composed of water and a water-soluble organic solvent. Preferably, the solvent further contains a wetting agent comprising a high-boiling organic solvent. Preferred examples of high-boiling organic solvents usable herein include: polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, propylene glycol, butylene glycol, 1,2,6-hexanetriol, thioglycol, hexylene glycol, glycerin, trimethylolethane, and trimethylolpropane; alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monomethyl ether acetate, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, diethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxybutanol, propylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-iso-propyl ether, propylene glycol mono-n-butyl ether, dipropylene glycol mono-n-butyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, dipropylene glycol mono-n-propyl ether, and dipropylene glycol mono-iso-propyl ether; urea; 2-pyrrolidone and N-methyl-2-pyrrolidone; 1,3-dimethyl-2-imidazolidinone; formamide; acetamide; dimethyl sulfoxide; sorbit; sorbitan; acetin; diacetin; triacetin; and sulfolane. They may be used alone or in combination of two or more.

The amount of the wetting agent added is preferably in the range of about 3 to 40% by weight, more preferably in the range of about 3 to 30% by weight, based on the ink composition.

The ink compositions to be used in the present invention may further contain a surfactant. Examples of surfactants include anionic surfactants, nonionic surfactants, and acetylene glycol surfactants. They may be used alone or as a mixture of two or more.

Specific examples of preferred acetylene glycol surfactants usable in the present invention include compounds represented by the following formula (a):

(a)



wherein $0 \leqq m+n \leqq 50$; and R^1, R^2, R^3, and R^4 each independently represent an alkyl group (preferably an alkyl group having 1 to 6 carbon atoms).

Among the compounds represented by formula (a), particularly preferred compounds include 2,4,7,9-tetramethyl-5-decyne-4,7-diol, 3,6-dimethyl-4-octyne-3,6-diol, and 3,5-dimethyl-1-hexyn-3-ol. Commercially available products may also be used as the acetylene glycol surfactant represented by the formula (a). Specific examples thereof include Surfynol 82, Surfynol 104, Surfynol 440, Surfynol 465, Surfynol 485, and Surfynol TG (all the above products being available from Air Products and Chemicals Inc.) and OLFINE STG and OLFINE E 1010 (tradenames: manufactured by Nissin Chemical Industry Co., Ltd.).

The amount of the surfactant added is preferably about 0.1 to 3% by weight, more preferably about 0.5 to 2% by weight, based on the ink composition. The surface tension of the ink compositions to be used in the present invention is generally not more than 45 mN/m, preferably 25 to 45 mN/m.

The ink compositions to be used in the present invention may further contain nozzle clogging preventives, preservatives or antimolds, antioxidants, electric conductivity adjustors, pH adjustors, solubilizers, viscosity modifiers, penetrants, surface tension modifiers, oxygen absorbers, etc.

Examples of preservatives or antimolds include sodium benzoate, pentachlorophenol sodium, 2-pyridinethiol-1-oxide sodium, sodium sorbate, sodium dehydroacetate, and 1,2-dibenzothiazolin-3-one (Proxel CRL, Proxel BDN, Proxel GXL, Proxel XL-2, and Proxel TN, manufactured by Zeneca Co., Ltd.).

Examples of pH adjustors, solubilizers, or antioxidants usable in the ink compositions include: amines, such as diethanolamine, triethanolamine, propanolamine, andmorpholine, and modification products thereof; inorganic salts, such as potassium hydroxide, sodium hydroxide, and lithium hydroxide; ammonium hydroxide; quaternary ammonium hydroxide, such as tetramethylammonium; salts of carbonic acid, such as potassium carbonate, sodium carbonate, and lithium carbonate; salts of phosphoric acid, such as potassium phosphate, sodium phosphate, and lithium phosphate; N-methyl-2-pyrrolidone; ureas, such as urea, thiourea, and tetramethylurea; allophanates, such as allophanate and methyl allophanate; biurets, such as biuret, dimethylbiuret, and tetramethylbiuret; and L-ascorbic acid and salts thereof.

According to the present invention, the other optional ingredients may be used alone, or alternatively a plurality of optional ingredients may be selected from the same category or different categories and used as a mixture.

According to the present invention, for each ink composition, the amounts of all the ingredients are preferably selected so that the ink composition has a viscosity of less than 10 mPa·s at 20° C.

Recording Method

The ink set according to the present invention may be used in a recording method comprising the step of depositing an ink composition onto a recording medium to perform printing.

According to another aspect of the present invention, there is provided an ink jet recording method comprising the steps of: ejecting droplets of an ink composition contained in the ink set according to the present invention; and depositing the droplets onto a recording medium to perform printing.

According to a further aspect of the present invention, there is provided a record produced by any one of these recording methods.

EXAMPLES

The following examples further illustrate the present invention, but should not be construed as limiting the scope of the present invention.

Evaluation Test A

Preparation of Ink Compositions

Ingredients specified in Table 1 were mixed together in a mixing ratio specified in Table 1. The resultant solutions were filtered under pressure through a membrane filter having a pore diameter of 1 μm to prepare magenta ink compositions 1a to 11a. In the following tables, the amount of each ingredient is in wt % of the ingredient based on the total weight of the ink composition. The balance consists of water. For ink compositions 6a to 11a as comparative examples, compounds represented by formulae (III) and (IV) were used as colorants, and, in addition, C.I. Acid Red 52 and C.I. Acid Red 249 were used as conventional magenta colorants for evaluation.

The concentration of the colorant in the ink composition was regulated so that the OD value of magenta as printed on Xerox 4024 paper (plain paper) (manufactured by Xerox Corp., U.S.A.) was 1.0.

TABLE 1

	Magenta ink										
	1a	2a	3a	4a	5a	6a (comp. ex.)	7a (comp. ex.)	8a (comp. ex.)	9a (comp. ex.)	10a (comp. ex.)	11a (comp. ex.)
Dye											
M-1	1			1				2.5		1	
M-4		1.5			1.2						1
M-10			1								
LM-4	1				2.8					0.8	
LM-11		2.0		3							5.2
LM-13			3.8						4.5		
C.I. Acid Red 52						3					
C.I. Acid Red 249							4				
Triethylene glycol monobutyl ether	10	10				10				10	10
Diethylene glycol monobutyl ether			10				10		10		
Polyethylene glycol monobutyl ether					10						
Diethylene glycol	10	10	10	10	10	10	10	10	10	10	10
Glycerin	10	10	10	10	10	10	10	10	10	10	10
Olfine E 1010		1		2			1				1
Olfine STG			1		0.5			1	1		
Triethanolamine	1	0.5	1		1	1	0.5	1	1	1	0.5
2-Pyrrolidone	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
KOH	0.1	0.1			0.1	0.1	0.1			0.1	0.1
EDTA	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Proxel XL-2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

Abbreviations used in Table 1 are as follows.

KOH represents potassium hydroxide.

EDTA represents dihydrogen disodium ethylenediaminetetraacetate (chelating agent).

Olfine E 1010 and Olfine STG are tradenames for acetylene glycol surfactants manufactured by Nissin Chemical Industry Co., Ltd.

Proxel XL-2 is a tradename for a preservative manufactured by Zeneca K.K.

Tests on Evaluation of Ink Compositions

The ink compositions thus obtained were evaluated by the following tests 1A to 4A using the following recording media (1) to (4). The recording medium (1) is the so-called "plain paper," and the recording media (2) to (4) are specialty recording media for ink jet printers.

(Recording Media)

(1) Xerox 4024 (Xerox Corp., U.S.A.)

(2) EPSON Superfine Paper (Epson Hanbai Corporation)

(3) EPSON Specialty Gloss Paper for photographs (Epson Hanbai corporation)

(4) EPSON Specialty Gloss Film (Epson Hanbai Corporation)

In the evaluation tests, an ink jet printer EM-900C (manufactured by Seiko Epson Corporation) was used.

The lightfastness was evaluated by a lightfastness test using a xenon fadeometer Ci35A (manufactured by Atlas Electric Device) as an acceleration tester for fastness to light.

Test 1A: Lightfastness of Magenta Ink Compositions

For themagenta ink compositions, the formation of blotted images (solid printing) was carried out on the recording media (1) to (4). Light was applied to the print samples by means of a xenon fadeometer Ci35A (manufactured by Atlas Electric Device) for 60 hr. In this case, hue (L*, a*, b*) was determined before and after light irradiation by means of a GRETAG densitometer (manufactured by GRETAG, Ltd.), followed by the determination of the difference between color before the test and color after the test, ΔE*ab, by equation (i). The lightfastness was evaluated from the results according to the following criteria.

$$\Delta E^*ab=[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2} \quad \text{(i)}$$

A: Color difference ΔE*ab of not more than 5

B: Color difference ΔE*ab of more than 5 to 10

C: Color difference ΔE*ab of more than 10 to 20

D: Color difference ΔE*ab of more than 20

Test 2A: Waterfastness of Magenta Ink Compositions

For the magenta ink compositions 1a to 11a, the formation of blotted images (solid printing) was carried out on the recording media (1) to (4), followed by drying to provide prints. Pure water was put dropwise onto the prints. One min after dropping of the pure water, the prints were inspected for marks of water droplets. The waterfastness of the ink compositions was evaluated from the results according to the following criteria.

A: Marks of water droplets were not left at all.

B: Marks of water droplets were not substantially left.

C: Marks of water droplets were somewhat left.

D: Marks of water droplets were considerably left.

Test 3A: Fastness of Magenta Ink Compositions to Moisture

For the magenta ink compositions 1a to 11a, outline (void) characters were printed on the recording media (1) to (4). The prints were dried, and allowed to stand for one day under an environment of 40° C. and 85% RH. After the standing, the prints were inspected for blurring of ink characters. The fastness of the ink compositions to moisture was evaluated from the results according to the following criteria.

A: Void portions were not blurred at all.

B: The characters were still legible, although void portions were somewhat blurred.

C: Void portions were considerably blurred, rendering the characters considerably illegible.

Test 4A: Storage Stability of Ink Compositions

The ink compositions were placed in glass sample bottles. The sample bottles were hermetically sealed, and allowed to stand at 70° C. for seven days. After the standing, each ink composition was dropped on a 1-μm filter, and the filter was inspected for the presence of sediment. In this case, properties of the ink compositions were also evaluated. The storage stability of the ink compositions was evaluated from the results according to the following criteria.

A: There was neither sediment nor a change in properties and color tone of ink.

B: Properties and color tone of ink somewhat changed, although there was no sediment.

C: There were sediment and a change in properties and color tone of ink.

The results of evaluation in the tests 1A to 4A were as summarized in Table 2.

TABLE 2

		Magenta ink										
		1a	2a	3a	4a	5a	6a	7a	8a	9a	10a	11a
Test 1A	Xerox 4024	A	A	A	A	A	C	C	B	A	B	A
	Superfine	A	A	A	A	A	C	C	B	A	B	A
	Specialty Gloss Paper	A	A	A	A	A	C	C	B	A	A	A
	Specialty Gloss Film	A	A	A	A	A	C	C	B	A	A	A
Test 2A	Xerox 4024	B	B	C	B	B	C	B	C	B	C	B
	Superfine	B	A	A	A	A	B	B	B	B	B	B
	Specialty Gloss Paper	A	A	A	A	A	B	B	B	B	B	B
	Specialty Gloss Film	A	A	A	A	A	B	B	B	B	B	B
Test 3A	Superfine	A	A	A	A	A	B	B	B	B	B	B
	Specialty Gloss Paper	A	A	A	A	A	C	C	B	B	B	B
	Specialty Gloss Film	B	A	A	B	B	C	C	B	B	B	B
Test 4A		A	A	A	A	A	B	B	A	B	A	B

Evaluation Test B

Preparation of Ink Compositions

Deep magenta ink compositions 1M to 9M and light magenta ink compositions 1LM to 8LM were prepared according to formulations specified in the following tables.

In the following tables, the amount of each ingredient is in wt % of the ingredient based on the total weight of the ink composition. The balance consists of ion-exchanged water. Dyes M-1 to M-10 and LM-1 to LM-15 are dyes having respective structures noted above.

TABLE 3

	Deep magenta ink								
	1M	2M	3M	4M	5M	6M (comp. ex.)	7M (comp. ex.)	8M (comp. ex.)	9M (comp. ex.)
Dye	(M-1) 2.0	(M-4) 2.7	(M-7) 3.5	(M-10) 1.0	(M-4) 2.5 (M-10) 2.5	(C.I. Acid Red 52) 2.0	(C.I. Direct Red 227) 4.0	(C.I. Reactive Red 180) 2.7	(C.I. Acid Red 32) 2.2
Glycerin	10	10	5	10	10	10	10	10	10
Diethylene glycol		11	5	5	5	13	13	13	13
Triethylene glycol	10		8						
Triethanolamine	1	1							
2-Pyrrolidone			2						
1,3-Dimethyl-2-imidazolidinone			5		8				
Urea				5					
Diethylene glycol monobutyl ether	10								
Triethylene glycol monobutyl ether		10		10		10	10	10	10
Dipropylene glycol monobutyl ether			10						
Olfine STG	0.5				3				
Olfine E 1010		1				1	1	1	1
Olfine E 104				0.5					
EDTA*	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Proxel XL-2**	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Benzotriazole***	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Potassium hydroxide	0.1	0.1			0.05				

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive

TABLE 4

	Light magenta ink							
	1LM	2LM	3LM	4LM	5LM	6LM (comp. ex.)	7LM (comp. ex.)	8LM (comp. ex.)
Dye	(LM-1) 1.5	(LM-4) 2.0	(LM-6) 3.0	(LM-9) 0.5	(LM-2) 2.0 (LM-10) 2.0	(C.I. Acid Red 52) 0.5	(M-1) 0.7	(C.I. Acid Red 32) 0.6
Glycerin	10	10	5	10	10	10	10	10
Diethylene glycol		13	5	5	5	15	15	15
Triethylene glycol	10		10					
Triethanolamine		1					0.5	0.5
2-Pyrrolidone	2							
1,3-Dimethyl-2-imidazolidinone			5		8			
Urea				5				
Diethylene glycol monobutyl ether	10							
Triethylene glycol monobutyl ether		10		10		10	10	10
Dipropylene glycol monobutyl ether			10					
Olfine STG	0.5				3			
Olfine E 1010		1				1	1	1
Olfine E 104				0.5				
EDTA*	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Proxel XL-2**	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Benzotriazole***	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Potassium hydroxide		0.1			0.05		0.05	0.05

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive

Tests on Evaluation of Ink Compositions

The ink compositions thus obtained were evaluated by the following tests 1B to 5B using the following recording media (1) to (4). The recording medium (1) is the so-called "plain paper," and the recording media (2) to (4) are specialty recording media for ink jet printers.

(Recording Media)

(1) Xerox 4024 (Xerox Corp., U.S.A.)

(2) EPSON Superfine Paper (Epson Hanbai Corporation)

(3) EPSON Specialty Gloss Paper for photographs (Epson Hanbai Corporation)

(4) EPSON Specialty Gloss Film (Epson Hanbai Corporation) In the evaluation tests, an ink jet printer PM-770C (manufactured by Seiko Epson Corporation) was used.

The lightfastness was evaluated by a lightfastness test using a xenon fadeometer Ci35W (manufactured by Atlas Electric Device) as an acceleration tester for fastness to light.

Test 1B: Lightfastness of Magenta Ink Compositions

For the deep and light magenta ink compositions, the formation of blotted images (solid printing) of single colors was carried out on the recording media (1) to (4).

These print samples were subjected to a 60-hr lightfastness test using a xenon fadeometer Ci35W (manufactured by Atlas Electric Device). The difference between the color before the test and the color after the test, ΔE*ab, was determined by equation (i), and evaluated according to the following criteria.

$$\Delta E^*ab=[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2} \quad \text{(i)}$$

A: Color difference ΔE*ab of not more than 5

B: Color difference ΔE*ab of more than 5 to 10

C: Color difference ΔE*ab of more than 10 to 20

D: Color difference ΔE*ab of more than 20

Test 2B: Test on Gas Resistance of Magenta Ink Compositions

The same print samples as used in the test 1B were evaluated for the resistance of the prints to ozone gas, sulfur dioxide gas (SO_2), and nitrogen dioxide gas (NO_2) by means of a constant rate flow type gas corrosion tester (manufactured by Yamazaki Seiki K.K.).

In the test on gas resistance, for each gas, an environment having a gas concentration of 1 ppm was provided, and each print sample was allowed to stand for 72 hr under each environment. The difference between the color before the test and the color after the test, ΔE*ab, was determined by equation (i), and evaluated according to the following criteria.

A: Color difference ΔE*ab of not more than 5 for all the test

B: Color difference ΔE*ab of more than 5 to 10 for at least one test

C: Color difference ΔE*ab of more than 10 for at least one test

The results of evaluation in the tests 1B and 2B were as summarized in Table 5.

TABLE 5

		Test 1B: Lightfastness Recording medium				Test 2B: Gas resistance Recording medium			
		(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Deep magenta ink	1M	B	A	A	A	A	A	A	A
	2M	B	A	A	A	A	A	A	A
	3M	B	A	A	A	A	A	A	A
	4M	B	C	B	A	A	A	A	A
	5M	A	A	A	A	A	A	A	A
	6M	D	D	D	D	A	D	B	D
	7M	C	D	C	B	A	B	B	B
	8M	C	C	B	B	A	B	A	A
	9M	A	A	A	A	A	D	D	D
Light magenta ink	1LM	B	B	B	A	A	A	A	A
	2LM	A	A	A	A	A	A	A	A
	3LM	A	A	A	A	A	A	A	A
	4LM	B	B	C	B	A	A	A	A
	5LM	A	A	A	A	A	A	A	A
	6LM	D	D	D	D	A	D	B	B
	7LM	B	B	B	A	A	A	A	A
	8LM	A	A	A	A	A	D	D	D

Test 3B: Lightfastness

Deep magenta ink compositions and light magenta ink compositions were loaded in combination as specified in Table 6 respectively into a deep magenta ink chamber and a light magenta ink chamber in an ink cartridge for PM-770C (Model IC5CL02, manufactured by Seiko Epson Corporation) to prepare ink sets 1b to 11b. Blotted images of red, blue, and composite black with a density of 70% were printed using the ink sets 1b to 11b on the recording media (1) to (4).

In this case, printing was carried out under conditions controlled such that the red with a density of 70% was constituted by the deep magenta ink, the light magenta ink, and the yellow ink, the blue with a density of 70% was constituted by the deep magenta ink, the light magenta ink, the deep cyan ink, and the light cyan ink, and the composite black with a density of 70% was constituted by the deep magenta ink, the light magenta ink, the deep cyan ink, the light cyan ink, the yellow ink, and the black ink.

The yellow ink, the deep cyan ink, the light cyan ink, and the black ink used were original inks in an ink cartridge for

TABLE 6

		Deep magenta ink	Light magenta ink
Ink Set	1b	1M	1LM
	2b	2M	2LM
	3b	3M	3LM
	4b	4M	4LM
	5b	5M	5LM
	6b (comp. ex.)	6M	6LM
	7b (comp. ex.)	7M	1LM
	8b (comp. ex.)	8M	1LM
	9b (comp. ex.)	8M	8LM
	10b (comp. ex.)	9M	9LM
	11b (comp. ex.)	1M	8LM

These print samples were subjected to a 60-hr lightfastness test using a xenon fadeometer Ci35W (manufactured by Atlas Electric Device). The difference between the color before the test and the color after the test, ΔE*ab, was

determined by equation (i) in the same manner as in test 1A, and evaluated according to the same criteria as used in the test 1B.

Test 4B: Gas Resistance

The same print samples as used in the test 3B were evaluated for the resistance of the prints to ozone gas, sulfur dioxide gas (SO_2), and nitrogen dioxide gas (No_2) by means of a constant rate flow type gas corrosion tester (manufactured by Yamazaki Seiki K.K.).

In the test on gas resistance, for each gas, an environment having a gas concentration of 1 ppm was provided, and each print sample was allowed to stand for 72 hr under each environment. The difference between the color before the test and the color after the test, ΔE*ab, was determined by equation (i), and evaluated according to the following criteria.

A: Color difference ΔE*ab of not more than 5 for all the tests

B: Color difference ΔE*ab of more than 5 to 10 for at least one test

C: Color difference ΔE*ab of more than 10 for at least one test

Test 5B: Bleeding

For the ink sets shown in Table 6, blotted images of each color were formed on the recording media (1) to (4). These print samples were inspected for color bleeding or uneven color mixing in boundaries of different colors. The bleeding was evaluated from the results according to the following criteria.

A: There was no bleeding.

B: There was color bleeding or uneven color mixing, in slight portion, on a level causing no practical problem.

C: There was significant color bleeding or uneven color mixing on a level causing slight practical problem.

D: There was severe color bleeding.

The evaluation results of the tests 3B to 5B were as summarized in Table 7.

TABLE 7

	Test 3B: Lightfastness					Test 4B: Gas resistance					Test 5B: Bleeding			
	Print with density	Recording medium				Print with density	Recording medium				Recording medium			
	70%	(1)	(2)	(3)	(4)	70%	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Ink	Red	B	A	A	A	Red	A	A	A	A	A	A	A	A
set 1b	Blue	B	A	A	A	Blue	A	A	A	A				
	Black	B	A	A	A	Black	A	A	A	A				
Ink	Red	B	A	A	A	Red	A	A	A	A	A	A	A	A
set 2b	Blue	B	A	A	A	Blue	A	A	A	A				
	Black	B	A	A	A	Black	A	A	A	A				
Ink	Red	B	A	A	A	Red	A	A	A	A	B	A	A	B
set 3b	Blue	B	A	A	A	Blue	A	A	A	A				
	Black	B	A	A	A	Black	A	A	A	A				
Ink	Red	B	C	B	A	Red	A	A	A	A	A	A	A	A
set 4b	Blue	B	B	A	A	Blue	A	A	A	A				
	Black	B	C	B	A	Black	A	A	A	A				
Ink	Red	A	A	A	A	Red	A	A	A	A	B	A	A	C
set 5b	Blue	A	A	A	A	Blue	A	A	A	A				
	Black	A	A	A	A	Black	A	A	A	A				
Ink	Red	D	D	D	D	Red	A	B	B	B	A	A	A	A
set 6b	Blue	A	B	B	B	Blue	A	C	C	C				
	Black	D	D	D	D	Black	A	C	C	C				
Ink	Red	C	D	D	B	Red	A	B	B	B	A	A	A	A
set 7b	Blue	C	C	C	C	Blue	A	C	C	C				
	Black	B	B	B	B	Black	A	B	B	B				
Ink	Red	B	D	D	B	Red	A	B	A	A	A	A	A	A
set 8b	Blue	B	C	B	A	Blue	A	C	B	C				
	Black	B	C	C	A	Black	A	B	B	B				
Ink	Red	B	D	D	B	Red	A	B	A	A	A	A	A	A
set 9b	Blue	C	C	C	D	Blue	A	C	B	C				
	Black	C	C	C	D	Black	A	C	B	C				
Ink	Red	A	A	A	A	Red	B	C	C	C	A	A	A	A
set 10b	Blue	D	D	D	D	Blue	B	C	C	C				
	Black	D	D	D	D	Black	B	C	C	C				
Ink	Red	B	A	A	A	Red	A	B	A	B	A	A	A	A
set 11b	Blue	B	C	C	D	Blue	A	B	B	B				
	Black	B	C	C	D	Black	A	B	A	B				

Evaluation Test C

Preparation of Ink Sets

Ink compositions were prepared according to formulations specified in the following tables, and were then used in combination to prepare ink sets 1c to 7c. In the following tables, the amount of each ingredient is in wt % of the ingredient based on the total weight of the ink composition. The balance consists of ion-exchanged water. Colorants Y-1 to Y-8, M-1 to M-10, LM-1 to LM-15, and C-1 to C-3 are colorants having respective structures noted above.

TABLE 8

Ink set 1c		Yellow	Deep magenta	Light magenta	Deep cyan	Light cyan
Dye	Yellow	(Y-1) 0.7 (Y-4) 2.8				
	Deep magenta		(M-1) 2.2			
	Light magenta			(LM-1) 1.8		
	Deep cyan				C.I. Direct Blue 199 3.5	
	Light cyan					C.I. Direct Blue 199 1.0
Glycerin		10	10	10	10	10
Triethylene glycol		8	5	10	5	10
Triethanolamine			1	0.3		
Diethylene glycol monobutyl ether		10				
Triethylene glycol monobutyl ether			10	10	10	10
Olfine STG		1				
Olfine E 1010			1	1	1	1
EDTA*		0.02	0.02	0.02	0.02	0.02
Proxel XL-2**		0.3	0.3	0.3	0.3	0.3
Benzotriazole***		0.01	0.01	0.01	0.01	0.01
Potassium hydroxide			0.1	0.03		

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive

TABLE 9

Ink set 2c		Yellow	Deep magenta	Light magenta	Deep cyan	Light cyan
Dye	Yellow	(Y-2) 1.0 (Y-4) 3.0				
	Deep magenta		(M-4) 2.4			
	Light magenta			(LM-1) 2.0		
	Deep cyan				C.I. Direct Blue 199 3.0	
	Light cyan					PFC2# 1
Diethylene glycol		5	5	5	5	5
Triethylene glycol		12	10	18	9	15
Triethanolamine		1	1			
2-Pyrrolidone			5	2		
Diethylene glycol monobutyl ether		10	10	10	10	10
Olfine E 1010			1	1	1	1
Olfine E 104		1				
EDTA*		0.02	0.02	0.02	0.02	0.02
Proxel XL-2**		0.3	0.3	0.3	0.3	0.3
Benzotriazole***		0.01	0.01	0.01	0.01	0.01
Potassium hydroxide		0.1				

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive
PFC2#: Projet Fast Cyan 2 (a product of Zeneca K.K.)

TABLE 10

Ink set 3c		Yellow	Deep magenta	Light magenta	Deep cyan	Light cyan
Dye	Yellow	(Y-1) 0.5 (Y-4) 2.0				
	Deep magenta		(M-8) 3.5			
	Light magenta			(LM-1) 3.0		
	Deep cyan				PFC2# 4.5	
	Light cyan					C.I. Direct Blue 86 1.5
Glycerin		8	8	5	10	5
Triethylene glycol		5	5	10	4	10
2-Pyrrolidone		5	5	5	5	5
Urea		5	5	5	5	5
Dipropylene glycol monobutyl ether		10	10	10	10	10

TABLE 10-continued

Ink set 3c	Yellow	Deep magenta	Light magenta	Deep cyan	Light cyan
Olfine STG	0.5	0.5	0.5	0.5	0.5
EDTA*	0.02	0.02	0.02	0.02	0.02
Proxel XL-2**	0.3	0.3	0.3	0.3	0.3
Benzotriazole***	0.01	0.01	0.01	0.01	0.01

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive
PFC2#: Projet Fast Cyan 2 (a product of Zeneca K.K.)

TABLE 11

Ink set 4c (comp. ex.)		Yellow	Deep magenta	Light magenta	Deep cyan	Light cyan
Dye	Yellow	(Y-1) 0.7 (Y-4) 2.8				
	Deep magenta		(M-1) 2.4			
	Light magenta			(M-1) 1.8		
	Deep cyan				C.I. Direct Blue 199 3.5	
	Light cyan					C.I. Direct Blue 199 1.0
Glycerin		10	10	10	10	10
Triethylene glycol		8	5	10	5	10
Triethanolamine			1	0.3		
Diethylene glycol monobutyl ether		10				
Triethylene glycol monobutyl ether			10	10	10	10
Olfine STG		1				
Olfine E 1010			1	1	1	1
EDTA*		0.02	0.02	0.02	0.02	0.02
Proxel XL-2**		0.3	0.3	0.3	0.3	0.3
Benzotriazole***		0.01	0.01	0.01	0.01	0.01
Potassium hydroxide			0.1	0.03		

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive

TABLE 12

Ink set 5c (comp. ex.)		Yellow	Deep magenta	Light magenta	Deep cyan	Light cyan
Dye	Yellow	(Y-1) 0.7 (Y-4) 2.8				
	Deep magenta		(LM-1) 6.0			
	Light magenta			(LM-1) 2.0		
	Deep cyan				C.I. Direct Blue 199 3.5	
	Light cyan					C.I. Direct Blue 199 1.0
Glycerin		10	10	10	10	10
Triethylene glycol		8	5	10	5	10
Triethanolamine			1	0.3		
Diethylene glycol monobutyl ether		10				
Triethylene glycol monobutyl ether			10	10	10	10
Olfine STG		1				
Olfine E 1010			1	1	1	1
EDTA*		0.02	0.02	0.02	0.02	0.02
Proxel XL-2**		0.3	0.3	0.3	0.3	0.3
Benzotriazole***		0.01	0.01	0.01	0.01	0.01
Potassium hydroxide			0.1	0.03		

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive

TABLE 13

Ink set 6c (comp. ex.)		Yellow	Deep magenta	Light magenta	Deep cyan	Light cyan
Dye	Yellow	C.I. Acid Yellow 23 2.0				
	Deep magenta		C.I. Reactive Red 180 2.4			
	Light magenta			(LM-1) 0.8		
	Deep cyan				C.I. Direct Blue 199 3.5	
	Light cyan					C.I. Direct Blue 199 0.9
Glycerin		10	10	10	10	10
Triethylene glycol		8	5	10	5	10
Triethanolamine			1	0.3		
Diethylene glycol monobutyl ether		10				
Triethylene glycol monobutyl ether			10	10	10	10
Olfine STG		1				
Olfine E 1010			1	1	1	1
EDTA*		0.02	0.02	0.02	0.02	0.02
Proxel XL-2**		0.3	0.3	0.3	0.3	0.3
Benzotriazole***		0.01	0.01	0.01	0.01	0.01
Potassium hydroxide			0.1	0.03		

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive

TABLE 14

Ink set 7c (comp. ex.)		Yellow	Deep magenta	Light magenta	Deep cyan	Light cyan
Dye	Yellow	(Y-5) 0.5 (Y-8) 2.8				
	Deep magenta		(M-1) 1.4			
	Light magenta			C.I. Acid Red 52 0.7		
	Deep cyan				C.I. Acid Blue 9 2.5	
	Light cyan					C.I. Direct Blue 199 1.0
Diethylene glycol		5	5	5	5	5
Triethylene glycol		12	10	18	9	15
Triethanolamine		1				
2-Pyrrolidone				2		
Diethylene glycol monobutyl ether		10	10	10	10	10
Olfine E 1010			1	1	1	1
Olfine E 104		1				
EDTA*		0.02	0.02	0.02	0.02	0.02
Proxel XL-2**		0.3	0.3	0.3	0.3	0.3
Benzotriazole***		0.01	0.01	0.01	0.01	0.01
Potassium hydroxide		0.1	0.1			

Note)
EDTA*: Sodium ethylenediamine tetraacetate (metal masking agent)
Proxel XL-2**: Preservative (a product of Zeneca K.K.)
Benzotriazole***: Rust preventive

Test on Evaluation of Ink Sets

The ink sets thus obtained were evaluated by the following tests 1C to 3C using the following recording media (1) to (4). The recording medium (1) is the so-called "plain paper," and the recording media (2) to (4) are specialty recording media for ink jet printers.

(Recording Media)

(1) Xerox 4024 (Xerox Corp., U.S.A.)

(2) EPSON Superfine Paper (Epson Hanbai Corporation)

(3) EPSON Specialty Gloss Paper for photographs (Epson Hanbai Corporation)

(4) EPSON Specialty Gloss Film (Epson Hanbai Corporation)

In the evaluation tests, an ink jet printer PM-770C (manufactured by Seiko Epson Corporation) was used.

The lightfastness was evaluated by a lightfastness test using a xenon fadeometer Ci35W (manufactured by Atlas Electric Device) as an acceleration tester for fastness to light.

Test 1C: Lightfastness

Each of the ink sets was loaded into an ink cartridge for PM-770C (Model IC5CL02, manufactured by Seiko Epson Corporation), and blotted images of red, blue, green, and composite black with a density of 70% were printed on the recording media (1) to (4).

In this case, printing was carried out under conditions controlled such that the red with a density of 70% was

constituted by the deep magenta ink, the light magenta ink, and the yellow ink, the blue with a density of 70% was constituted by the deep magenta ink, the light magenta ink, the deep cyan ink, and the light cyan ink, the green with a density of 70% was constituted by the yellow ink, the deep cyan ink, and the light cyan ink, and the composite black with a density of 70% was constituted by the deep magenta ink, the light magenta ink, the deep cyan ink, the light cyan ink, the yellow ink, and the black ink. The black ink used was an original ink for PM-770C.

These print samples were subjected to a 60-hr lightfastness test using a xenon fadeometer Ci35W (manufactured by Atlas Electric Device). The difference between the color before the test and the color after the test, ΔE^*_{ab}, was determined by equation (i), and evaluated according to the following criteria.

$$\Delta E^*_{ab}=[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2} \quad \text{(i)}$$

A: Color difference ΔE^*_{ab} of not more than 5
B: Color difference ΔE^*_{ab} of more than 5 to 10
C: Color difference ΔE^*_{ab} of more than 10 to 20
D: Color difference ΔE^*_{ab} of more than 20
The results were as summarized in Tables 15.

TABLE 15

	Test 1C: Lightfastness				
		Recording medium			
	Print with density 70%	(1)	(2)	(3)	(4)
Ink set 1c	Red	A	A	A	A
	Blue	A	A	A	A
	Green	A	A	A	A
	Black	A	A	A	A
Ink set 2c	Red	A	A	A	A
	Blue	A	A	A	A
	Green	A	A	A	A
	Black	A	A	A	A
Ink set 3c	Red	A	A	A	A
	Blue	A	A	A	A
	Green	A	A	A	A
	Black	A	A	A	A
Ink set 4c	Red	B	B	B	B
	Blue	B	C	C	C
	Green	A	A	A	A
	Black	D	D	D	D
Ink set 5c	Red	A	A	A	A
	Blue	A	A	A	A
	Green	A	A	A	A
	Black	A	A	A	A
Ink set 6c	Red	C	C	C	C
	Blue	B	B	B	B
	Green	D	D	D	D
	Black	B	B	B	C
Ink set 7c	Red	D	D	D	D
	Blue	D	D	D	D
	Green	D	D	D	D
	Black	D	D	D	D

Test 2C: Color Reproduction Range

The ink sets prepared above were loaded into ink cartridges for PM-770C, and, for each of these ink sets, a patch pattern with gradation of 100 density levels was printed on the recording medium (3) for each of yellow, magenta, cyan, red, blue, and green. For the patches, lightness (L*) and hue (a*, b*) were measured. a* was plotted as X axis, b* as Y axis, and L* as Z axis to determine a color solid space (a color reproduction range).

The color reproduction range of the original ink set for PM-770C was presumed to be 100% and was compared with the color reproduction range of each ink set sample.

Test 3C: Recovery from Clogging

Each of the ink sets 1b to 7b was loaded into a printing head of PM-770C, and allowed to stand without capping the printing head under an environment of 40° C. for one month. After the standing for one month, the number of cleaning operations required for all the nozzles to normally eject the ink compositions in the ink set was counted, and the recovery from clogging was evaluated according to the following criteria.

A: Recovered by repeating the cleaning operation twice or less
B: Recovered by repeating the cleaning operation three to five times
C: Recovered by repeating the cleaning operation six to ten times
D: Not recovered even by repeating the cleaning operation ten times

The results of evaluation in the tests 2C and 3C were as summarized in Table 16.

TABLE 16

	Ink set							
	1c	2c	3c	4c	5c	6c	7c	PM-770C
Test 2C: Color reproduction range	105%	101%	110%	100%	88%	94%	110%	100%
Test 3C: Recovery from clogging	A	A	A	A	D	B	A	A

Evaluation Test D

Preparation of Ink Sets

Ingredients specified in Tables 1 to 6 were mixed together in a mixing ratio specified in Tables 17 to 21. The resultant solutions were filtered under pressure through a membrane filter having a pore diameter of 1 μm to prepare ink compositions, and were then used in combination to prepare ink sets 1d to 10d. In the following tables, the amount of each ingredient is in wt % of the ingredient based on the total weight of the ink composition. The balance consists of water. The ink sets id to 6d are ink sets of examples of the present invention, and the ink sets 7d to 10d are comparative ink sets.

TABLE 17

	Ink set 1d					Ink set 2d				
	M	LM	Y	C	LC	M	LM	Y	C	LC
M-6	2.5									
M-10						1.5				

TABLE 17-continued

	Ink set 1d					Ink set 2d				
	M	LM	Y	C	LC	M	LM	Y	C	LC
LM-2	1.0									
LM-11						1.5				
C.I. Acid Red 52										
C.I. Acid Red 249										
C.I. Direct Yellow 86			0.4					1.0		
C.I. Direct Yellow 132			0.8					2.0		
C.I. Acid Yellow 23										
C.I. Direct Blue 86										
C.I. Direct Blue 199				2.0					2.5	
C.I. Acid Blue 9										
Triethylene glycol monobutyl ether										
Diethylene glycol monobutyl ether	10		10	10						
Polyethylene glycol monobutyl ether	10		10	10		10		10	10	
Diethylene glycol	10		10	10		10		10	10	
Olfine E 1010										
Olfine STG						2.0		2.0	2.0	
Triethanolamine	1.0		1.0	1.0		0.5		0.5	0.5	
EDTA	0.01		0.01	0.01		0.01		0.01	0.01	
Proxel XL-2	0.3		0.3	0.3		0.3		0.3	0.3	

TABLE 18

	Ink set 3d					Ink set 4d				
	M	LM	Y	C	LC	M	LM	Y	C	LC
M-3	2.0									
M-7						2.5				
LM-1		1.5								
LM-4							1.0			
C.I. Acid Red 52										
C.I. Acid Red 249										
C.I. Direct Yellow 86			2.0					0.5		
C.I. Direct Yellow 132			0.8					0.5		
C.I. Acid Yellow 23										
C.I. Direct Blue 86				2.0	0.5				2.5	1.0
C.I. Direct Blue 199										
C.I. Acid Blue 9										
Triethylene glycol monobutyl ether	10	10	10	10	10					
Diethylene glycol monobutyl ether						12	12	12	12	12
Polyethylene glycol monobutyl ether	10	10	10	10	10	10	10	10	10	10
Diethylene glycol	10	10	10	10	10	10	10	10	10	10
Olfine E 1010	1.0	1.0	1.0	1.0	1.0					
Olfine STG						0.5	0.5	0.5	0.5	0.5
Triethanolamine	1.0	1.0	1.0	1.0	1.0	0.5	0.5	0.5	0.5	0.5
EDTA	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Proxel XL-2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

TABLE 19

	Ink set 5d					Ink set 6d				
	M	LM	Y	C	LC	M	LM	Y	C	LC
M-3	3.5									
M-7						2.5				
LM-1		2.5								
LM-4							2.0			
C.I. Acid Red 52										
C.I. Acid Red 249										
C.I. Direct Yellow 86			1.0					1.0		
C.I. Direct Yellow 132			2.0					1.5		
C.I. Acid Yellow 23										
C.I. Direct Blue 86										
C.I. Direct Blue 199				2.5	1.0				3.5	0.9
C.I. Acid Blue 9										
Triethylene glycol monobutyl ether						10	10	10	10	10
Diethylene glycol monobutyl ether										
Polyethylene glycol monobutyl ether	10	10	10	10	10	10	10	10	10	10
Diethylene glycol	1.0	1.0	1.0	1.0	1.0	10	10	10	10	10

TABLE 19-continued

	Ink set 5d					Ink set 6d				
	M	LM	Y	C	LC	M	LM	Y	C	LC
Olfine E 1010	1.0	1.0	1.0	1.0	1.0					
Olfine STG										
Triethanolamine	1.0	1.0	1.0	1.0	1.0	0.5	0.5	0.5	0.5	0.5
EDTA	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Proxel XL-2	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3

TABLE 20

	Ink set 7d (comp. ex.)					Ink set 8d (comp. ex.)				
	M	LM	Y	C	LC	M	LM	Y	C	LC
C.I. Acid Red 52	1.5					2.5	0.7			
C.I. Acid Red 249	1.5									
C.I. Direct Yellow 86										
C.I. Direct Yellow 132										
C.I. Acid Yellow 23			2.0					1.5		
C.I. Direct Blue 86										
C.I. Direct Blue 199										
C.I. Acid Blue 9				3.5					2.5	1.0
Triethylene glycol monobutyl ether	12		12	12						
Diethylene glycol monobutyl ether										
Polyethylene glycol monobutyl ether	10		10	10		10	10	10	10	10
Diethylene glycol	10		10	10		10	10	10	10	10
Olfine E 1010										
Olfine STG						2.0	2.0	2.0	2.0	2.0
Triethanolamine	1.0		1.0	1.0		0.5	0.5	0.5	0.5	0.5
EDTA	0.01		0.01	0.01		0.01	0.01	0.01	0.01	0.01
Proxel XL-2	0.3		0.3	0.3		0.3	0.3	0.3	0.3	0.3

TABLE 21

	Ink set 9d (comp. ex.)					Ink set 10d (comp. ex.)				
	M	LM	Y	C	LC	M	LM	Y	C	LC
M-4	2.0					1.0				
LM-7	0.5						0.5			
C.I. Acid Red 52						1.5	1.5			
C.I. Acid Red 249	0.5									
C.I. Direct Yellow 86			1.0							
C.I. Direct Yellow 132								2.0		
C.I. Acid Yellow 23			1.0					1.0		
C.I. Direct Blue 86										
C.I. Direct Blue 199				3.0						
C.I. Acid Blue 9									3.5	0.8
Triethylene glycol monobutyl ether						10	10	10	10	10
Diethylene glycol monobutyl ether	10		10	10						
Polyethylene glycol monobutyl ether	10		10	10		10	10	10	10	10
Diethylene glycol	10		10	10		10	10	10	10	10
Olfine E 1010	1.0		1.0	1.0						
Olfine STG						0.5	0.5	0.5	0.5	0.5
Triethanolamine	1.0		1.0	1.0		0.5	0.5	0.5	0.5	0.5
EDTA	0.01		0.01	0.01		0.01	0.01	0.01	0.01	0.01
Proxel XL-2	0.3		0.3	0.3		0.3	0.3	0.3	0.3	0.3

Abbreviations used in Tables 17 to 21 are as follows.

EDTA represents dihydrogen disodium ethylenediaminetetraacetate (chelating agent).

Olfine E 1010 and Olfine STG are tradenames for acetylene glycol surfactants manufactured by Nissin Chemical Industry Co., Ltd.

Proxel XL-2 is a tradename for a preservative manufactured by Zeneca K.K.

Tests on Evaluation of Ink Compositions

The ink compositions thus obtained were evaluated by the following tests 1D to 3D using the following recording media (1) to (4). The recording medium (1) is the so-called "plain paper," and the recording media (2) to (4) are specialty recording media for ink jet printers.

(Recording Media)

(1) Xerox 4024 (Xerox Corp., U.S.A.)

(2) EPSON Superfine Paper (Epson Hanbai Corporation)

(3) EPSON Specialty Gloss Paper for photographs (Epson Hanbai Corporation)

(4) EPSON Specialty Gloss Film (Epson Hanbai Corporation)

In the evaluation tests, an ink jet printer PM-770C (used with a cartridge for six colors; manufactured by Seiko Epson

Corporation) and an ink jet printer MJ-930C (used with a cartridge for four colors; manufactured by Seiko Epson Corporation) were used.

The lightfastness was evaluated by a lightfastness test using a xenon fadeometer Ci35W (manufactured by Atlas Electric Device) as an acceleration tester for fastness to light.

Test 1D: Lightfastness

For ink sets 3d to 6d, 8d, and 10d, deep magenta, light magenta, yellow, deep cyan, and light cyan inks were loaded into respective ink chambers in an ink cartridge for PM-770C (manufactured by Seiko Epson corporation), and blotted images of magenta, yellow, cyan, red, blue, green, and composite black were printed on the recording media (1) to (4).

In this case, printing was carried out under conditions controlled such that the red was constituted by the deep magenta ink, the light magenta ink, and the yellow ink, the blue was constituted by the deep magenta ink, the light magenta ink, the deep cyan ink, and the light cyan ink, the green was constituted by the yellow ink, the deep cyan ink, and the light cyan ink, and the composite black was constituted by the deep magenta ink, the light magenta ink, the yellow ink, the deep cyan ink, the light cyan ink, and the black ink.

For ink sets 1d, 2d, 7d, and 9d, yellow, and cyan inks were loaded into respective ink chambers in an ink cartridge for MJ-930C (manufactured by Seiko Epson Corporation), and blotted images of magenta, yellow, cyan, red, blue, green, and composite black were printed on the recording media (1) to (4).

These print samples were irradiated with light for 60 hr by means of a xenon fadeometer Ci35A (manufactured by Atlas Electric Device). In this case, hue (L*, a*, b*) was determined before and after light irradiation by means of a GRETAG densitometer (manufactured by GRETAG, Ltd.), followed by the determination of the difference between color before the test and color after the test, ΔE*ab, by equation (i). The lightfastness was evaluated from the results according to the following criteria.

$$\Delta E^*_{ab}=[(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{1/2} \quad \text{(i)}$$

A: Color difference ΔE^*_{ab} of not more than 5

B: Color difference ΔE^*_{ab} of more than 5 to 10

C: Color difference ΔE^*_{ab} of more than 10 to 20

D: Color difference ΔE^*_{ab} of more than 20

Test 2D: Bleeding

For each ink set, blotted images of each color were formed on the recording media (1) to (4). These print samples were inspected for color bleeding or uneven color mixing in boundaries of different colors. The bleeding was evaluated from the results according to the following criteria.

A: There was no bleeding.

B: There was color bleeding or uneven color mixing, in slight portion, on a level causing no practical problem.

C: There was significant color bleeding or uneven color mixing on a level causing slight practical problem.

D: There was severe color bleeding.

Test 3D: Recovery from Nozzle Clogging

Inks in each ink set were loaded into a printing head. After the ejection of the inks through the nozzles of the head without any problem was confirmed by inspection of prints, the printer was stopped, and allowed to stand without capping the printing head under an environment of 40° C. for one month. After the standing for one month, the power supply of the printer was turned on to perform cleaning operations until all the nozzles could normally eject the ink composition. The necessary number of cleaning operations was counted. The recovery from nozzle clogging was evaluated from the results according to the following criteria.

A: Recovered by conducting the cleaning operation twice or less

B: Recovered by repeating the cleaning operation three to five times

C: Recovered by repeating the cleaning operation six to ten times

D: Not recovered even by repeating the cleaning operation ten times

The results of the tests 1D to 3D were as summarized in Table 22.

TABLE 22

	Ink set									
	1d	2d	3d	4d	5d	6d	7d	8d	9d	10d
Test 1D										
Xerox 4024	A	A	A	A	A	A	C	C	B	B
Superfine	A	A	A	A	A	A	C	C	B	B
Specialty Gloss Paper	A	A	A	A	A	A	C	C	B	B
Specialty Gloss Film	A	A	A	A	A	A	C	C	B	B
Test 2D										
Xerox 4024	A	A	A	A	A	A	B	B	A	A
Superfine	A	A	A	A	A	A	A	A	A	A
Specialty Gloss Paper	A	A	A	A	A	A	A	A	A	A
Specialty Gloss Film	A	A	A	A	A	A	A	A	A	A
Test 3D	A	A	A	A	A	A	A	A	A	A

Evaluation Test E: Color Reproduction

For yellow, magenta, and cyan inks used in the ink sets in the evaluation tests C and D, color calculation was carried out using a spectrophotometer U-3300 (manufactured by Hitachi, Ltd.) to determine the hue (L*, a*, b*) of the inks. For magenta and cyan inks, the hue was also determined on the light inks. The measurement was carried out under conditions of D65 as a standard light source, field of view 2 degrees, and measurement wavelength 300 to 800 nm.

The results were as shown in Table 23 and FIG. **1**. In FIG. **1**, inks according to the present invention had hues falling within respective portions surrounded by dotted lines. When the hues of the inks fall within the respective portions surrounded by dotted lines, good color reproduction and good color tone can be realized.

TABLE 23

Ink set		a*	b*	Ink set		a*	b*
1c	Y	−5	95	4c	Y	−5	95
	M	75	−5		M	75	−5
	LM	17	−3		LM	35	−3
	C	−45	−55		C	−45	−50
	LC	−13	−22		LC	−13	−20
2c	Y	−1	90	5c	Y	−5	95
	M	72	−8		M	46	−6
	LM	20	5		LM	17	−3
	C	−42	−50		C	−42	−45
	LC	−10	−16		LC	−10	−12
3c	Y	−5	83	6c	Y	3	107
	M	69	4		M	65	−5
	LM	28	9		LM	9	0
	C	−36	−45		C	−45	−50
	LC	−10	−18		LC	−13	−18

TABLE 23-continued

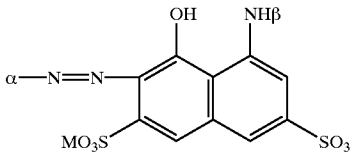
Ink set		a*	b*	Ink set		a*	b*
1d	Y	10	72	7c	Y	2	87
	M	78	10		M	49	−1
	C	−37	−48		LM	42	−17
2d	Y	12	85		C	−48	−68
	M	70	6		LC	−13	−20
	C	−35	−44	7d	Y	3	107
3d	Y	17	85		M	80	−24
	M	70	−5		C	−40	−60
	LM	15	−3	8d	Y	8	98
	C	−30	−42		M	87	−36
	LC	−12	−21		LM	40	−17
4d	Y	5	60		C	−46	−55
	M	79	−6		LC	−28	−28
	LM	10	−1	9d	Y	10	88
	C	−32	−44		M	75	7
	LC	−17	−27		C	−40	−43
5d	Y	12	85	10d	Y	5	90
	M	69	4		M	81	−2
	LM	30	9		LM	53	−28
	C	−35	−44		C	−54	−69
	LC	−13	−20		LC	−20	−26
6d	Y	10	80				
	M	73	−8				
	LM	22	6				
	C	−45	−50				
	LC	−13	−18				

What is claimed is:

1. An ink set comprising first and second magenta ink compositions different from each other in color density, wherein the first magenta ink composition has a higher color density than the second magenta ink composition which has a lower color density,

said first magenta ink composition with higher color density containing as a colorant a compound represented by formula (III)

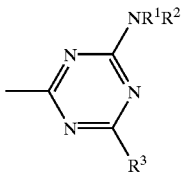
(III)



wherein

α represents a C_1–C_4 alkyl or alkoxy group or an OH—, SO_3H—, or COOM-substituted phenyl or naphthyl group;

β represents a hydrogen atom or a group represented by formula



wherein

R^1 represents a hydrogen atom or an OH— or COOH-substituted C_1–C_4 alkyl group,

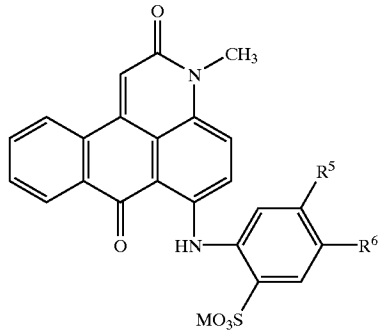
R^2 represents an OH—, OCH_3—, OC_2H_5—, SO_3M—, or COOM-substituted C_1–C_4 alkyl or phenyl group, and

R^3 represents an OH, COOH, or NHR^4 wherein R^4 represents an SO_3M— or COOH-substituted C_1–C_4 alkyl group; and

M represents a hydrogen atom, lithium, sodium, potassium, ammonium or an organic amine,

said second magenta ink composition with lower color density containing as a colorant a compound represented by formula (IV):

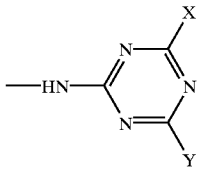
(IV)



wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine;

R^5 represents a hydrogen atom, a chlorine atom or a group represented by formula



wherein

X represents an anilino group substituted by at least one SO_3M and

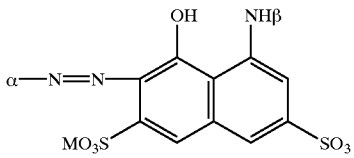
Y represents OH, a chlorine atom, or a morpholino group; and

R^6 represents a hydrogen atom, a chlorine atom, SO_3M, or a C_1–C_4 alkyl group.

2. The ink set according to claim **1**, wherein the first magenta ink composition with higher color density contains 1.5 to 3.5% by weight of the compound represented by formula (III) and the second magenta ink composition with lower color density contains 1 to 3% by weight of the compound represented by formula (IV).

3. A magenta ink composition comprising as a colorant (a) the compound represented by formula (III)

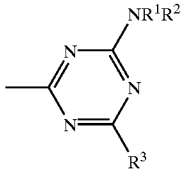
(III)



wherein

α represents a C_1–C_4 alkyl or alkoxy group or an OH—, SO_3H—, or COOM-substituted phenyl or naphthyl group;

β represents a hydrogen atom or a group represented by formula



wherein

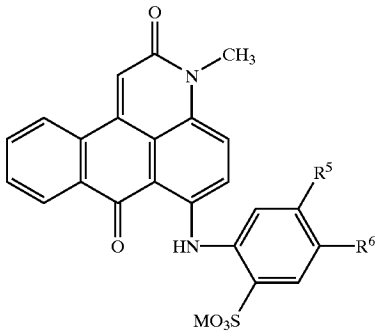
R^1 represents a hydrogen atom or an OH— or COOH-substituted C_1–C_4 alkyl group,

R^2 represents an OH—, OCH_3—, OC_2H_5—, SO_3M—, or COOM-substituted C_1–C_4 alkyl or phenyl group, and

R^3represents an OH, COOH, or NHR^4 wherein R^4 represents an SO_3M— or COOH-substituted C_1–C_4 alkyl group; and

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine, and (b) the compound represented by formula (IV)

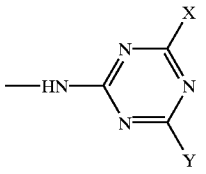
(IV)



wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine;

R^5 represents a hydrogen atom, a chlorine atom or a group represented by formula



wherein

X represents an anilino group substituted by at least one SO_3M and

Y represents OH, a chlorine atom, or a morpholino group; and

R^6 represents a hydrogen atom, a chlorine atom, SO_3M, or a C_1–C_4 alkyl group,

said compounds represented by formulas (III) and (IV) being present in the magenta ink composition in a weight ratio of 1:1 to 1:5.

4. The magenta ink composition according to claim **3**, wherein the colorant is contained in an amount of 0.5 to 5% by weight based on the total amount of the ink composition.

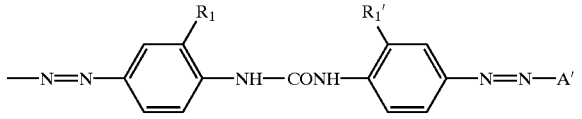
5. An ink set comprising the magenta ink composition according to claim **3**.

6. The ink set according to claim **1**, which further comprises a yellow ink composition and a cyan ink composition.

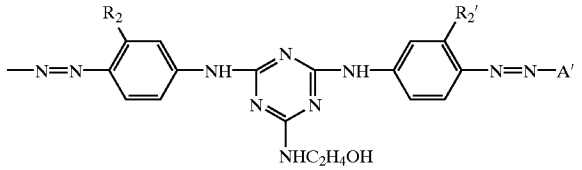
7. An ink set comprising: a yellow ink composition; first and second magenta ink compositions different from each other in color density, the first magenta ink composition having a higher color density than the second magenta ink composition which has a lower color density; and first and second cyan ink compositions different from each other in color density, the first cyan ink composition having a higher color density than the second cyan ink composition which has a lower color density,

said yellow ink composition containing as a colorant a compound represented by formula (I) and/or a compound represented by formula (II):

(I)



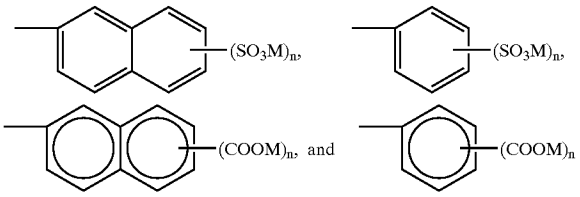
(II)



wherein

R_1, R_1', R_2, and R_2' each independently represent CH_3 or OCH_3; and

A and A' each independently represent a group having a structure selected from the group consisting of



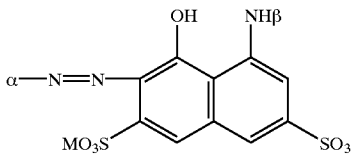
wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine; and

n is an integer of 1 or 2,

said first magenta ink composition with higher color density containing as a colorant a compound represented by formula (III):

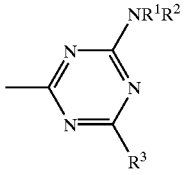
(III)



wherein

α represents a C_1–C_4 alkyl or alkoxy group or an OH—, SO_3H—, or COOM-substituted phenyl or naphthyl group;

β represents a hydrogen atom or a group represented by formula



wherein

R^1 represents a hydrogen atom or an OH— or COOH-substituted C_1–C_4 alkyl group,

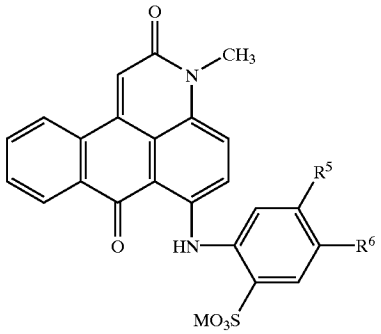
R^2 represents an OH—, OCH_3—, OC_2H_5—, SO_3M—, or COOM-substituted C_1–C_4 alkyl or phenyl group, and

R^3 represents an OH, COOH, or NHR^4 wherein R^4 represents an SO_3M— or COOH-substituted C_1–C_4 alkyl group; and

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine,

and/or a compound represented by formula (IV):

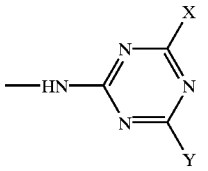
(IV)



wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine;

R^5 represents a hydrogen atom, a chlorine atom or a group represented by formula



wherein

X represents an anilino group substituted by at least one SO_3M and

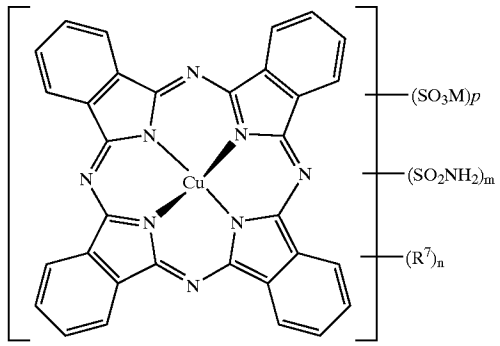
Y represents OH, a chlorine atom, or a morpholino group; and

R^6 represents a hydrogen atom, a chlorine atom, SO_3M, or a C_1–C_4 alkyl group,

said second magenta ink composition with lower color density containing as a colorant the compound represented by formula (III) and/or the compound represented by formula (IV),

said first cyan ink composition with higher color density and said second cyan ink composition with lower color density each containing as a colorant a compound represented by formula (V):

(V)



wherein

R^7 represents OH, COOM, or R^8COOM wherein R^8 represents a C_4–C_9 alkyl group; and

p, m, and n are each 0 to 4 with (p+m+n)=4.

8. The ink set according to claim **7**, wherein the content of the compound represented by formula (I) and/or the compound represented by formula (II) in the yellow ink composition is 0.3 to 4% by weight in total.

9. The ink set according to claim **7**, wherein the yellow ink composition cons 0.3 to 4.0% by weight of the compound reseted by formula (I) and/or the compound represented by formula (II), first the magenta ink composition with higher color density contains 1.0 to 4.0% by weight of the compound represented by formula (II), the second magenta ink composition with lower color density contains 0.5 to 3.0% by weight of the compound represented by formula (IV), the first cyan ink composition with higher color density contains 1.0 to 4.0% by weight of the compound represented by formula (V), and the second cyan ink composition with lower color density contains 0.5 to 3.0% by weight of the compound represented by formula (V).

10. The ink set according to claim **7**, wherein the first magenta ink composition with higher color density contains 1.5 to 3.5% by weight of the compound represented by formula (III) and the second magenta ink composition with lower color density contains 1 to 3% by weight of the compound represented by formula (IV).

11. The ink set according to claim **7**, wherein the first magenta ink composition with higher color density and the second magenta ink composition with lower color density each contain the compound represented by formula (III) and the compound represented by formula (IV) in a weight ratio of 1:1 to 1:5.

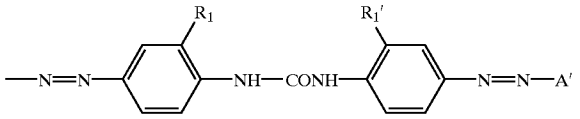
12. The ink set according to claim **7**, wherein the first cyan ink composition with higher color density contains 2.5 to 4.5% by weight of the compound represented by formula (V) and the second cyan ink composition with lower color density contains 0.4 to 1.5% by weight of the compound represented by formula (V).

13. The ink set according to claim **7**, wherein the hue (a*, b*) is in the range of (−20 to 20, 60 to 110) for the yellow ink composition, in the range of (50 to 90, −20 to 10) for the first magenta ink composition with higher color density, in the range of (10 to 40, −10 to 10) for the second magenta ink composition with lower color density, in the range of (−50 to −30, −60 to −40) for the first cyan ink composition with higher color density, and in the range of (−30 to −10, −30 to −10) for the second cyan ink composition with lower color density.

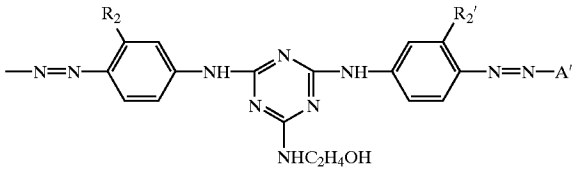
14. An ink set comprising a yellow ink composition, a magenta ink composition, and a cyan ink composition,

said yellow ink composition containing as a colorant the compound represented by formula (I) and/or the compound represented by formula (II),

(I)



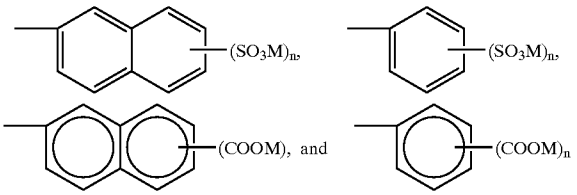
(II)



wherein

R_1, R_1', R_2, and R_2' each independently represent CH_3 or OCH_3; and

A and A' each independently represent a group having a structure selected from the group consisting of



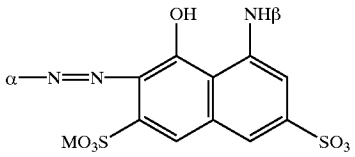
wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine; and

n is an integer of 1 or 2,

said magenta ink composition containing as a colorant (b) the compound represented by formula (III)

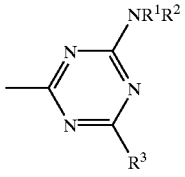
(III)



wherein

α represents a C_1–C_4 alkyl or alkoxy group or an OH—, SO_3H—, or COOM-substituted phenyl or naphthyl group;

β represents a hydrogen atom or a group represented by formula



wherein

R^1 represents a hydrogen atom or an OH— or COOH-substituted C_1–C_4 alkyl group,

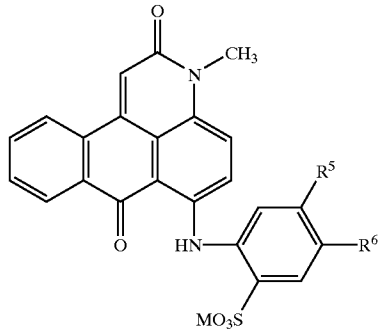
R^2 represents an OH—, OCH_3—, OC_2H_5—, SO_3M—, or COOM-substituted C_1–C_4 alkyl or phenyl group, and

R^3 represents an OH, COOH, or NHR^4 wherein R^4 represents an SO_3M— or COOH-substituted C_1–C_4 alkyl group; and

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine,

and/or (b) the compound represented by formula (IV)

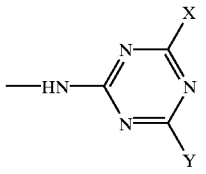
(IV)



wherein

M represents a hydrogen atom, lithium, sodium, potassium, ammonium, or an organic amine;

R^5 represents a hydrogen atom, a chlorine atom or a group represented by formula



wherein

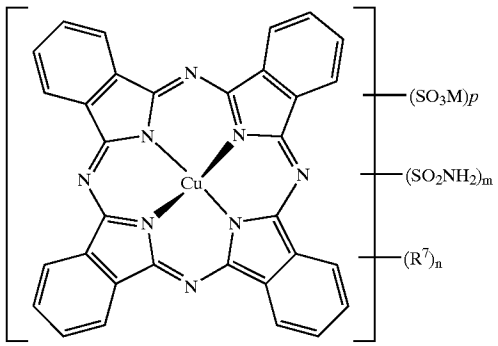
X represents an anilino group substituted by at least one SO_3M and

Y represents OH, a chlorine atom, or a morpholino group; and

R^6 represents a hydrogen atom, a chlorine atom, SO_3M, or a C_1–C_4 alkyl group,

said cyan ink composition containing as a colorant the compound represented by formula (V)

(V)



wherein

R^1 represents OH, COOM, or R^8COOM wherein R^8 represents a C_4–C_9 akyl group; and

p, m, and n are each 0 to 4 with (p+m+n)=4.

15. The ink set according to claim 14, wherein

the yellow ink composition contains as the colorant 0.3 to 4.0% by weight in total of the compound represented by formula (I) and/or the compound represented by formula (II),

the magenta ink composition contains as the colorant 1.0 to 4.0% by weight in total of the compound represented by formula (III) and/or the compound represented by formula (IV), and

the cyan ink composition contains as the colorant 1.0 to 4.0% by weight of the compound represented by formula (V).

16. The ink set according to claim 14, wherein the magenta ink composition contains the compound represented by formula (III) and the compound represented by formula (IV) in a weight ratio of 1:1 to 1:5.

17. The ink set according to claim 11, wherein the hue (a*, b*) is in the range of (−20 to 20, 60 to 110) for the yellow ink composition, in the range of (50 to 90, −20 to 10) for the magenta ink composition, and in the range of (−50 to −30, −60 to −40) for the cyan ink composition.

18. The ink set according claim 6, which further comprises a black ink composition.

19. The ink set according to claim 6, wherein each of the first magenta, second magenta, yellow and cyan ink compositions further comprises a surfactant.

20. A method for recording comprising:

(a) providing the ink set according to claim 1; and

(b) depositing onto a recording medium to perform printing each of the first magenta and second magenta ink compositions.

21. A method for ink jet recording comprising:

(a) providing the ink set according to claim 1; and

(b) ejecting droplets of each of the first magenta and second magenta ink compositions and depositing the droplets onto a recording medium to perform printing.

22. A record produced by the recording method of claim 20.

23. A method for recording comprising:

(a) providing the ink set according to claim 7; and

(b) depositing onto a recording medium to perform printing each of the yellow, first magenta, second magenta, first cyan and second cyan ink compositions.

24. A method for ink jet recording comprising:

(a) providing the ink set according to claim 7; and

(b) ejecting droplets of each of the yellow, first magenta, second magenta, first cyan and second cyan ink compositions and depositing the droplets onto a recording medium to perform printing.

25. A record produced by the recording method of claim 23.

26. A method for recording comprising:

(a) providing the ink set according to claim 14; and

(b) depositing onto a recording medium to perform printing each of the yellow, magenta and cyan ink compositions.

27. A method for ink jet recording comprising:

(a) providing the ink set according to claim 14; and

(b) ejecting droplets of each of the yellow, magenta and cyan ink compositions and depositing the droplets onto a recording medium to perform printing.

28. A record produced by the recording method of claim 26.

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